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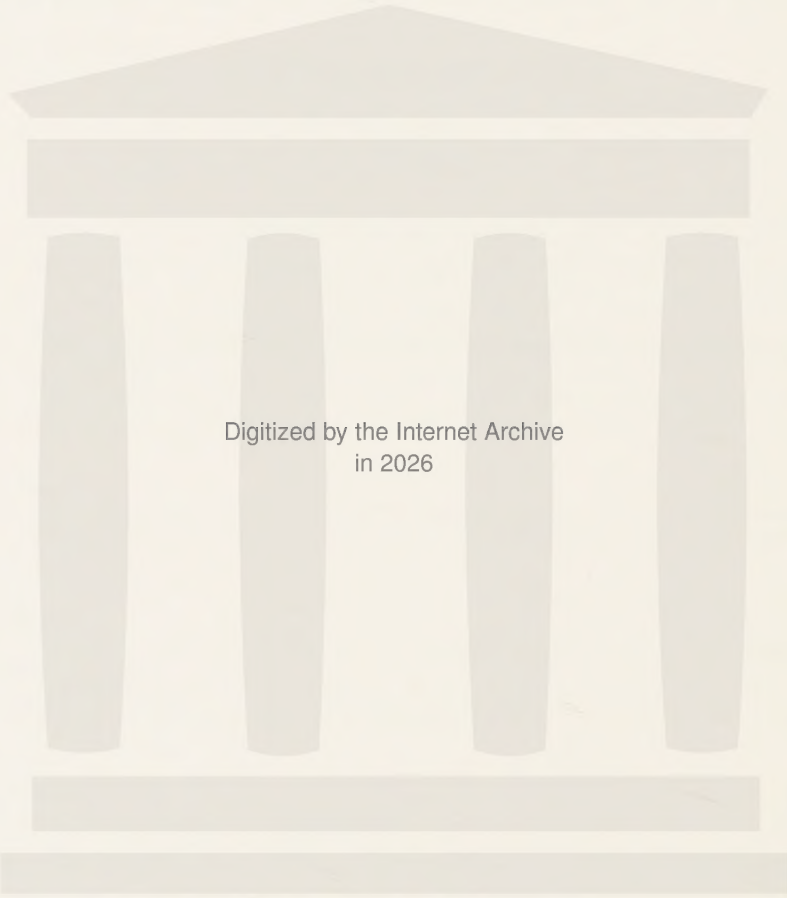
on

NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN

held in

The Department of Metallurgy
The University of Sheffield

Tuesday, 20th September to Thursday, 22nd September, 1960



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I. Melting, Sintering and Working

THE MECHANICAL PROPERTIES OF SOME DUCTILE NIOBIUM AND TANTALUM BASE ALLOYS PREPARED BY ELECTRON BEAM MELTING

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(Received June 3rd, 1960)

SUMMARY

This paper presents the results of studies made on a relatively small number of niobium and tantalum base alloys. Using impact transition temperature as a criterion for initial evaluation, a number of alloys have been selected for high temperature tensile and creep rupture tests as well as fabrication studies. These data are being obtained at the present time, and more complex modifications of these alloys are being explored.

Tantalum alloys containing more than 20% tungsten are very brittle and this limits the usefulness of the combination. Present investigations in our laboratory, as well as at others, are directed toward the development of more complex alloys to take advantage of the exceptional ductility exhibited by tantalum base alloy systems.

Niobium alloy development is still in its infancy. Although the electron beam process restricts the number of combinations of alloying elements that can be used, there is a good possibility that, in addition to tungsten, molybdenum, and zirconium, rhenium and hafnium may materially improve high temperature properties. Economic reasons, however, restrict the amounts of these latter two additions that can be used at present. Although at other laboratories there are higher strength niobium alloys being prepared than the ones discussed here, they are considerably less fabricable and ductile. The efforts of this investigation have been directed toward the development of alloys with good fabricability rather than stronger alloys with severe fabrication problems.

INTRODUCTION

Commercial scale electron beam melting has made possible the routine production of exceptionally high purity refractory metal alloys. This high purity is essential if ductility and fabricability in such alloys are to be combined with reasonably good mechanical properties at elevated temperatures.

The first alloy development programme at Stauffer-Temescal was conducted on the molybdenum and tungsten systems. Unfortunately, the initial results indicated that electron beam melting produced no significant improvement in the impact transition temperature of even very pure molybdenum and tungsten. Since the magnitude of this particular property is related directly to problems in the fabrication of these metals, particularly in welding, the alloy development effort was shifted to niobium and tantalum base alloys whose impact properties are considerably better. The purity of these alloys is also critical, not only with respect to the interstitial

impurities such as oxygen, nitrogen, carbon, and hydrogen, but also with respect to volatile metallic impurities such as iron and nickel.

Electron beam melting provides a means of producing these exceptionally high purity alloys, but there are two main disadvantages: (1) because it produces a metal or alloy of higher purity with accompanying greater ductility, the net result is generally a weaker alloy; and (2) there are certain common elements which cannot be alloyed with tungsten, niobium, tantalum, and molybdenum because they are lost by evaporation during the melting process. These elements, chromium, titanium, vanadium, and, to a lesser degree zirconium, appear to be useful primarily in imparting oxidation resistance to niobium and tantalum base alloys.

The first disadvantage can be rectified by the addition of more of the non-volatile alloying elements to replace the effect of the lost interstitials and volatile metals. The second disadvantage appears to be minor in the production of the ductile niobium and tantalum base alloys in view of the evidence that these alloys are ductile *only* if the volatile metals are substantially eliminated.

The development effort at Stauffer-Temescal was directed toward the production of alloys of tantalum and niobium possessing good high temperature strength coupled with good fabricability. Further, the alloys were developed so that they could be forged or worked at steel forging temperature where, with only ordinary precautions, oxidation losses are small. This is in contrast to the numerous alloys developed in recent years having good high temperature strength, but with very limited fabricability.

Since a major objective in all high temperature alloy programmes is to form sheet stock, another criterion for a suitable alloy is that it can be either warm or cold rolled to sheet. Much of the high loss in the usual fabrication of refractory metal alloys has been due to rolling at high temperature. Low temperature rolling not only reduces the losses, but produces better surfaced sheet.

As a matter of general practice in this alloy development work, Charpy V notch impact tests were made on an alloy as soon as practicable. The transition temperature for the brittle to ductile failure was determined for each alloy. At temperatures above the impact transition temperature, fabrication has generally been successful. Below the transition temperature, fabrication has always been unsuccessful.

Considerable effort has been expended to develop a multipurpose alloy for high temperature use; one that would have high strength, high oxidation resistance, and good fabricability. This combination of requirements appears to be complicating many alloy development programmes unnecessarily, since the oxidation resistance is incompatible with the other properties. The programme described here has been directed toward attaining high strength with good fabricability. It is believed that good oxidation resistance will only come with coatings and that an alloy with a good combination of the three properties is of doubtful feasibility.

PROCEDURE

Tantalum-tungsten alloys

It has been reported in the literature that tantalum and tungsten form a continuous series of solid solutions with one another. However, until quite recently, the only fabricable alloy of tantalum-tungsten was a 92% tantalum-8% tungsten alloy.

With the advent of electron beam melting, alloys of tantalum-tungsten up to 20% tungsten have been prepared.

The 20% tungsten alloy presented fabrication problems, so, for production operations, the tungsten content was reduced. It appears at the present time that 85% tantalum-15% tungsten is marginally useful as a production item, but 90% tantalum-10% tungsten is completely fabricable and reproducible in its properties at production levels of several tons per month.

The 90% tantalum-10% tungsten alloy produced by the electron beam furnace is in the form of ingots 4-6 in. in diameter and approximately 40 in. long. These are forged by conventional drop hammer techniques after they have been heated to 2,200°F. The forging temperature must be maintained in the temperature range 2,000-2,200°F since the material has very high strength, even at these temperatures. Under these conditions no difficulty has been experienced in forging the alloy. It can be both upset and pierced.

For sheet production, the ingots are forged into suitable slabs, the oxide skin is removed by either grinding or machining and the slab is vacuum annealed at 2,600°F for one hour. Rolling commences after the annealed slab has been reheated to 500°F.

TABLE I
ULTIMATE TENSILE STRENGTH OF TANTALUM-TUNGSTEN ALLOYS

<i>Alloy</i>	<i>Temperature °F (°C)</i>	<i>Ultimate tensile strength (p.s.i.)</i>
85% Ta-15% W forged bar	5300 (2927)	2040
	5060 (2793)	3720
	5060 (2793)	3600
	4880 (2693)	4050
90% Ta-10% W forged bar	5300 (2927)	1,920
	5030 (2777)	2,470
	4865 (2685)	3,230
	4850 (2677)	3,230
	R.T.	146,000 20% Elong.
90% Ta-10% W sheet 0.060 in. thick as-rolled-90% R.A.	1598 (870)	81,400*
	1604 (873)	75,700*
	1795 (980)	72,400*
	1795 (980)	75,700*
	2008 (1098)	59,100*
	2015 (1102)	61,100*

* All failed outside gauge length. Estimated elongation about 6-10%.

TABLE II
ULTIMATE TENSILE STRENGTH OF A 90% Ta-10% W ALLOY

<i>Temperature °F</i>	<i>Strain rate per sec</i>	<i>Ultimate tensile strength (p.s.i.)</i>
2000	0.0055	41,600
2400	0.0055	44,100
2600	0.0047	37,600
2800	0.005	35,400
3000	0.0056	26,900

As a general rule, one reannealing operation is sufficient to roll a plate from $\frac{1}{2}$ in. down to 0.060 in. thick. After rolling, the sheet is generally annealed at 2,400°F for one hour for maximum fabricability.

High temperature tensile tests performed in vacuum have been made on 90% tantalum-10% tungsten and 85% tantalum-15% tungsten alloys. The results are presented in Tables I and II and in Fig. 1.

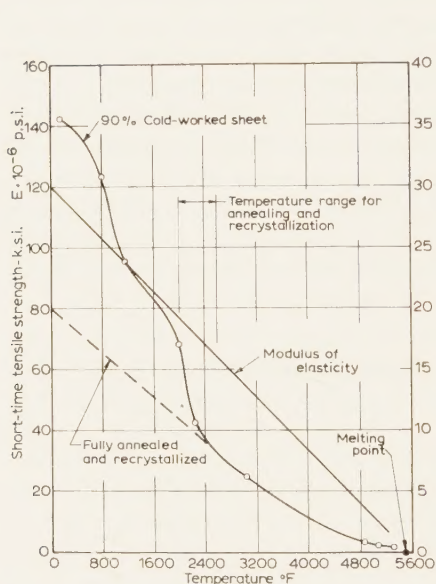


Fig. 1. Mechanical properties of electron beam melted 90% Ta-10% W alloy.



Fig. 2. Annealing of a 90% Ta-10% W alloy.

Tests to determine the recrystallization temperature of 90% tantalum-10% tungsten have been performed on sheet that has been cold rolled to 90% reduction in area. The material is about 50% recrystallized in 15 min at 2,200°F (1,200°C) and is fully recrystallized in 15 min at 2,500°F (1,370°C). (see Fig. 2)

Niobium alloys

In the very high temperature range, tantalum and tungsten are the only readily available metals, but in mid-range the candidates based on melting point multiply rapidly; niobium, tungsten, tantalum, molybdenum, and, possibly hafnium, zirconium, titanium, vanadium and chromium enter into consideration. With electron beam melting, niobium, tungsten, tantalum, molybdenum, and zirconium are about the only possible metals that can be used. The others, with the exception of hafnium, are too volatile. Hence, various combinations of niobium, tungsten, tantalum, molybdenum, and sometimes, small amounts of zirconium have been melted into alloy systems and evaluated.

Impact tests at room temperature can eliminate many candidates. A completely

brittle fracture at room temperature indicates that the alloy will roll only at high temperature. The transition curve is determined for each alloy. An alloy with an impact transition above about 500°F is rejected.

As a general rule, it is found that 15% tungsten and 4% molybdenum represent the practical limits for alloying with niobium. If the indicated limits are exceeded, it is found that the ductile brittle transition will be about 500°F. Tantalum additions do not materially affect the impact properties of niobium, although it is reported that additions of up to 30% tantalum materially improve the oxidation resistance of niobium. Tungsten additions are also reported to improve the oxidation resistance of niobium.

Therefore, in determining suitable niobium alloys the contents of tungsten, molybdenum, tantalum and small amounts of other alloying elements are balanced so as to obtain an alloy that has the maximum high temperature strength consistent with a high strength-to-weight ratio and ease of fabrication. Oxidation resistance is not considered specifically in the judgment of alloys.

Considerable work has been performed on various combinations of niobium, tantalum, molybdenum and tungsten. Many alloys have been eliminated owing to high transition temperatures and it is possible that some alloys worthy of further study have been eliminated by this technique. However, because of the complexity of the systems involved, it is thought that this is a reasonable first screening process (see Fig. 3).

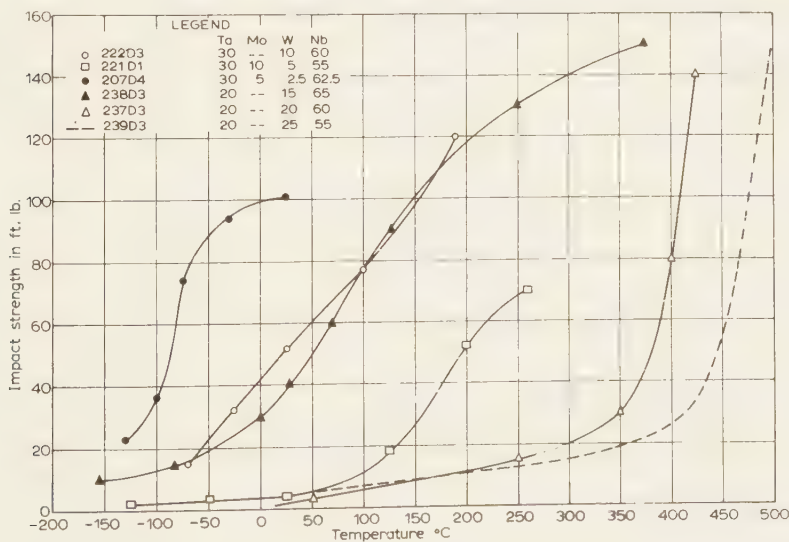


Fig. 3. Keyhole impact strength of niobium base alloys.

Tables III-VI list a number of niobium alloys that are either under investigation or have been subjected to preliminary screening. Table V gives the results of tests on some modified (grain refined) alloys. Tables VI and VII refer to alloys of the same general composition of 60% niobium, 30% tantalum and 10% other metals.

TABLE III
MECHANICAL PROPERTIES OF SOME NIOBIUM ALLOYS AFTER FORGING AT 2,000°F

Alloy number	Composition %			Impact strength at room temp. (ft.-lb.)	V notch or keyhole	Ultimate strength (p.s.i.)	Yield strength (p.s.i.)	R.A. %	Elong %
	Nb	Ta	Mo	W					
205 D3	68.5	30	—	1.5	231	V	65,200	86	17
206 D3	67.75	30	1.5	0.75	267	V	79,500	57	16
207 D4	62.5	30	5.0	2.5	37	V	90,600	59	18
221 D3	55.0	30	10.0	5.0	2	V	87,900	75	33
223 D3	82.0	10	3.0	3.0	171	V	65,900	70	38
199 D3	67.0	30	3.0	—	—	—	42,000	84	18
204 D3	65.0	30	—	5.0	—	—	73,700	79	18
197 D3	70.0	30	—	—	—	—	96,700	79	18
222 D3	60.0	30	—	10.0	52	K	125,600	36	16

TABLE V
MECHANICAL TESTS ON NIOBIUM BASE ALLOYS

Alloy	Coupon	Atmosphere	Temp. °F	Strain rate per sec	Ultimate strength (p.s.i.)	Yield strength (p.s.i.)	$E \times 10^{-4} (p.s.i.)$
Modified 60% Nb-30% Ta-10% W as cold rolled	1	Helium	2,000	0.0059	45,800	39,600	12.7
	2	Helium	2,000	0.0060	46,700	40,900	12.8
	3	Helium	2,200	0.0056	39,400	33,800	11.7
	4	Helium	2,400	0.0059	24,200	21,700	10.3
60% Nb-30% Ta-10% W as cold rolled	10	Helium	2,000	0.0056	43,000	38,000	13.8
	13	Helium	2,200	0.0056	36,500	32,700	11.3
	12	Helium	2,400	0.0067	21,000	18,600	8.9
	11	Helium	*	0.0067	24,400	20,300	9.8
	7	Air	2,000	0.0046	22,300	15,400	9.6
Modified 60% Nb-30% Ta-10% W annealed	8	Air	2,000	0.005	21,900	15,200	9.7
	9	Air	2,000	0.005	23,800	16,000	11.4
	14	Air	2,000	0.010	21,100	15,000	12.3
60% Nb-30% Ta-10% W annealed	15	Air	2,000	0.0083	22,000	14,900	13.5
	16	Air	2,200	0.0083	20,100	14,600	8.4
	17	Air	2,200	0.008	19,500	13,400	9.6

* Material was heated to 2,600°F, for 5 sec, then dropped to 2,200°F, held for 15 sec and tested.

TABLE IV

MECHANICAL PROPERTIES OF SOME NIOBIUM ALLOYS ANNEALED FOR 1 h, 2,000°F

Alloy number	Composition %				Ultimate strength (p.s.i.)	Yield strength (p.s.i.)	R.A. %	Elong. %
	Nb	Ta	Mo	W				
205 D3	68.5	30	—	1.5	49,200	38,800	79	33
206 D3	67.75	30	1.5	0.75	45,500	36,200	80	47
207 D4	62.5	30	5.0	2.5	85,200	77,500	67	23
223 D3	82.5	10	3.0	3.0	65,900	57,100	70	38
221 D3	55.0	30	10.0	5.0	59,300	—	—	—
199 D3	67.0	30	3.0	—	58,200	51,800	78	38
204 D3	65.0	30	—	5.0	61,900	56,400	71	25
222 D3	60.0	30	—	10.0	78,900	72,300	66	35.5
238 D3	65.0	20	—	15.0	97,400	—	56	27
237 D3	60.0	20	—	20.0	127,800	—	45	26.5
239 D3	55.0	20	—	25.0	130,900	—	10.2	12.5

TABLE VI

THE MECHANICAL PROPERTIES AT ROOM TEMPERATURE OF SOME DUCTILE NIOBIUM BASE ALLOYS

Room temperature mechanical properties of some improved niobium base alloys which can be forged to plate at 2,000°F and cold rolled to sheet.

Treatment	Alloy number	Temperature	Ultimate strength (p.s.i.)	Yield strength (p.s.i.)	Elong. %	$E \cdot 10^{-6} (p.s.i.)$
Forged bar stock – stress relieved for 1 h at 2,200°F	280 D3	R.T.	112,600	102,000	3.5	35.2
	284 D3	R.T.	99,100	89,900	16.5	—
Sheet 0.060 in. thick – as-rolled	280 D3	R.T.	148,600	—	2.1	—
	284 D3	R.T.	145,700	—	5.0	—
	ST-41	R.T.	138,100	—	5.0	—
Sheet 0.060 in. thick – stress relieved for 1 h at 2,200°F	280 D3	R.T.	100,600	—	15.0	—
	284 D3	R.T.	95,800	—	17.0	—
	ST-41	R.T.	104,500	—	13.0	—

TABLE VII

MECHANICAL PROPERTIES AT 2,400°F OF NIOBIUM BASE ALLOYS (SHEET)

Alloy number	Description	Strain rate per sec	Ultimate strength (p.s.i.)	Yield strength (p.s.i.)	$E \cdot 10^{-6} (p.s.i.)$
280 D3	*Stress relieved	0.0067	23,700	20,500	13.7
284 D3	As-rolled	0.005	23,800	22,300	11.3
ST-41	*Stress relieved	0.0054	26,300	22,100	14.7

* Stress relieved 1 h at 2,400°F.

PRACTICAL ASPECTS OF SINTERING TUNGSTEN AND MOLYBDENUM

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(Received June 7th, 1960)

SUMMARY

Manufacturing procedures for the preparation of tungsten and molybdenum powders together with the method of pressing the powders in a mould and direct sintering the pressed bars at high temperatures are given. A description is given of the method of sintering, in particular, molybdenum in a hydrogen-water vapour atmosphere at about $1,750^{\circ}\text{C}$ and of the continuous pressing, partial sintering and casting technique developed to meet demands for relatively large size plate and sheet.

Brief reference is made to the preparation of alloys by sintering in the presence of a liquid phase and of pseudo alloys by the infiltration technique.

The commercial development of tungsten and molybdenum has, from the beginning, been closely associated with the lamp and electronic industries. The present day manufacture of tungsten and molybdenum wire, by pressing the metal powder in a mould, direct sintering the pressed ingots at high temperature, swaging and drawing to wire, is based on developments originated by COOLIDGE^{1,2} in 1909.

PREPARATION OF TUNGSTEN POWDER

In the manufacture of tungsten powder only two ores, wolframite ($(\text{Fe}, \text{Mn})\text{WO}_4$) and scheelite (CaWO_4) are of commercial importance and they are supplied as concentrates in the form of coarse particles to large lumps.

With the exception of iron, manganese and calcium, tungsten concentrates contain only a small percentage of other elements and representative analyses of some typical concentrates from different parts of the world are given in Table I³.

Initial treatment of the concentrates comprises grinding by ball-milling. In the case of wolframite, steel ball-mills with steel balls may be used, but for scheelite, porcelain mills with either porcelain or flint balls are necessary to avoid iron contamination. In general, it is common practice to mill until 90-95% of the product passes a 150 mesh. In this physical condition the ore concentrates are ready for chemical treatment.

The initial stage in the preparation of metallic tungsten is the separation of tungstic acid from the other constituents in the ore, the methods used depending on the type of ore.

One process consists of fusing the ore with sodium carbonate, the resulting sodium tungstate being extracted with water. The fusion mixture is kept at approximately 800°C for several hours in a reverberatory type furnace with continuous agitation

TABLE I

Type of ore	Source	WO ₃	FeO	MnO	CaO	MgO	SiO ₂	Al ₂ O ₃
Wolframite	Spain	66.34	12.83	9.89	0.14	0.05	3.91	3.69
	China	68.30	10.29	10.70	0.20	0.09	1.95	0.41
	Australia	72.50	16.80	7.70	—	—	—	—
Scheelite	Australia	78.15	—	—	19.40	0.11	1.39	0.21
	South Africa	72.53	0.80	0.39	18.49	0.11	3.56	0.35
	Canada	74.85	1.90	0.39	18.73	0.20	1.19	0.66

Type of ore	Source	SnO ₂	CuO	MoO ₃	TiO ₂	Ta ₂ O ₅ Nb ₂ O ₅	Sb ₂ O Bi ₂ O ₃	As, S, P	Other elements
Wolframite	Spain	1.17	0.05	Trace	0.03	0.17	0.23	0.52	—
	China	1.64	0.02	0.03	0.5	1.06	0.14	0.34	0.24
	Australia	0.63	0.21	—	—	—	—	0.70	—
Scheelite	Australia	—	Nil	Nil	Trace	—	Trace	0.10	—
	South Africa	Trace	—	2.76	—	—	—	0.03	—
	Canada	Trace	—	0.39	—	0.09	Trace	0.45	—

to ensure complete oxidation of the iron and manganese. The following reactions take place:



The resulting product is then removed from the furnace and allowed to cool. The cooled fused mass is crushed and the sodium tungstate extracted by leaching with water.

An alternative method treats wolframite with strong caustic soda or potash solution. The ore, in quantities of 2,000–4,000 kg, may be charged into a steel tank, the requisite quantity of caustic soda added and the charge heated to boiling point by either external or internal means. Ores of high purity decompose readily, but an excess of 50% caustic soda is required to bring about rapid decomposition with low grade ores. The mixture is boiled with constant stirring for 4–8 hours, then diluted to twice its volume to cause further precipitation of the iron and manganese hydroxides and to prevent separation of sodium tungstate crystals.

The sodium tungstate resulting from wolframite is then generally converted to calcium tungstate by adding calcium chloride to the solution,



The white precipitate is thoroughly washed by decantation. The resulting calcium tungstate may then be treated in a similar manner to scheelite.

It is common practice³ to decompose the scheelite direct with hydrochloric acid in

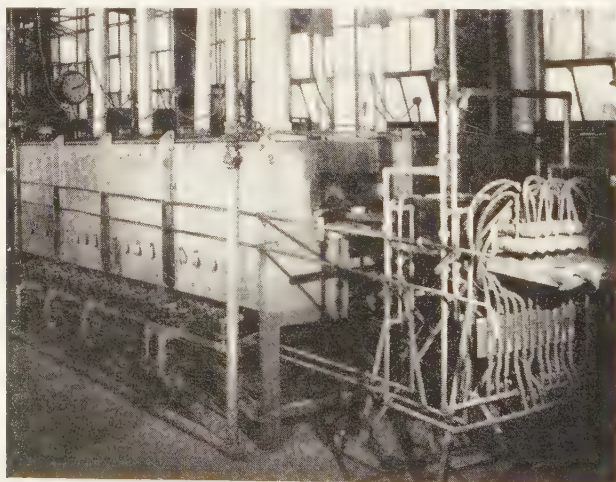
rubber-lined steel tanks. The vessel is fitted with a rubber-coated mechanical stirrer and a rubber-lined discharge valve at the base of the dome-shaped bottom of the vessel. For each kg of ore, 1 to 1.5 litres of conc. hydrochloric acid is required. This is run into the vessel, the stirrer started and the charge slowly introduced. The solution is boiled for about 3 h by injecting dry steam into the liquid. The steam is then shut off, and nitric acid is added to ensure highest efficiency in recovery of WO_3 . As the reaction may be violent, the addition is made slowly and continued until the reaction ceases, then the charge is boiled for a further half-hour to drive off all gaseous products of the oxidising process. The vessel is then filled with water, stirred for a further 5 min and the sludge allowed to settle. After settling, the liquor is siphoned off, the sludge residue consisting of tungstic acid (H_2WO_4) and insoluble materials, such as silica. The sludge is then washed free of soluble impurities such as calcium chloride by introducing boiling water.

This sludge may contain 98–99% of WO_3 or as little as 80% depending on the grade of ore used, the chief impurities being undecomposed ore, silica and silicates, cassiterite, iron and calcium.

The sludge now undergoes further purification, which may consist of extracting the WO_3 with ammonia followed by filtration and evaporation of the solution to form white crystals of ammonium paratungstate.

The crystals may now, if sufficiently pure, be decomposed by heat, or for further purification dissolved in a potash solution forming potassium tungstate from which tungstic oxide is precipitated by the addition of hydrochloric acid. The oxide is then washed and dried.

Conversion of the blue oxide to metal powder is generally a single-stage reduction, whereas the reduction of the yellow oxide to powder is generally a two-stage process, the first producing WO_2 followed by conversion of the brown oxide to metal powder. The reduction is carried out in oxygen-free dry hydrogen.



Courtesy of The General Electric Company Limited of England

Fig. 1. Gas-fired furnace for reducing WO_3 to metal powder.

The reduction is usually carried out in gas-fired or electrically heated furnaces fitted

with tubes of a heat-resisting alloy; the tubes may be round or rectangular in section. The oxide is fed through the tubes in boats of semicircular or rectangular cross-section to fit the furnace tubes. The gas-fired furnaces, which are built of fire-brick, are about 13–20 feet long and may contain up to 20 reduction tubes supported at intervals along their length. The tubes have an internal diameter or width of $1\frac{1}{2}$ –8 inches. A typical gas-fired furnace is shown in Fig. 1. A temperature gradient is maintained from one end of the furnace to the other; for first reduction this is usually from about 500°C at the feed end to 700°C at the discharge end, and for the second stage 600°C to 850°C. The boats are fed in the opposite direction to the hydrogen flow, so that the water-vapour concentration of the gas in contact with the powder decreases as reduction proceeds.

The conditions of reduction, such as temperature, rate of hydrogen flow, depth of oxide in boat, time, have an important bearing on the particle size of the powder produced. Thus, actual conditions of reduction are determined by the type of powder required, which for most purposes ranges from 0.6–6 micron.

PREPARATION OF MOLYBDENUM POWDER

Molybdenum is widely dispersed throughout the earth, though only two minerals, molybdenite (MoS_2) and wulfenite (PbMoO_4) can be considered as commercial ores. Nearly 90% of the world's supply is obtained from the United States, where the most important single source is the molybdenite deposit at Climax, Colorado. This deposit, up to 1946, yielded 85% of the world's supply. Since the war, however, a proportion of the molybdenum coming from America has been obtained as a by-product from copper concentration processes.

In the Climax deposit the molybdenite is found finely dispersed throughout the ore, and fine grinding followed by flotation is necessary to separate the mineral from the gangue. The method of concentration employs a flotation reagent consisting of pine oils, hydrocarbons and a synthetic wetting agent. Further concentration steps yield 1 ton of final product, in terms of MoS_2 , from about 150 tons of original mill feed. A typical analysis of the concentrate is shown in Table II⁴.

TABLE II
TYPICAL ANALYSIS OF CONCENTRATE

	%
Total molybdenum	56.00
Molybdenum oxide	0.06
S	37.80
Pb	0.04
Cu	0.18
Zn	0.06
Fe	0.38
SiO_2	4.50
Al_2O_3	0.28
CaO	0.06
MgO	0.08
As	trace
P	0.03

The molybdenum sulphide is converted to oxide by roasting in circular hearth-type furnaces; the operation requires no external fuel except for preheating after a shut-

down. Temperatures are controlled by drawing a large excess of air horizontally across the hearth.

Molybdc oxide begins to sublime at approximately 600°C and melts at approximately 800°C, so that too high a temperature results in excessive loss by volatilisation. The product, known as technical molybdc oxide, has the composition given in Table III⁴.

TABLE III
TECHNICAL MOLYBDC OXIDE

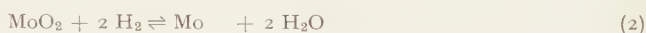
	%
Molybdc oxide	79-90
Copper (max.)	0.50
Sulphur (max.)	0.25
Residue (mainly SiO ₂)	Remainder

This forms the raw material for subsequent operations.

Pure molybdc oxide is made by volatilising the technical grade in a single-hearth doughnut-type electric furnace having a hearth temperature of approximately 1,000°C. The volatilised oxide passes through a metal flue and is collected in filter bags. It is a fine, light product containing approximately 99.975% molybdenum trioxide.

Anhydrous sodium molybdate is manufactured by dissolving the technical oxide in caustic soda, filtering, evaporating, crystallising and drying. Ammonium molybdate is made in a similar way and includes a metal grade which is the purest compound of molybdenum commercially available. Commercial ferromolybdenum is generally made by the Thermit process.

The pure molybdc oxide and ammonium molybdate are used for the production of fine powders. The reduction to metal is similar to that used for tungsten, and is often carried out in two steps:

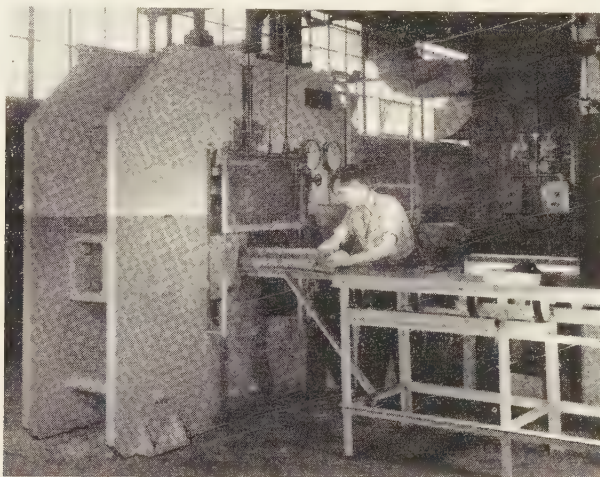


This double reduction is generally favoured because it avoids the formation of a coarse metal powder through the action of water vapour produced by the reaction. The temperature of reduction can be varied, but generally stage 1 is carried out at about 600°-700°C and stage 2 at about 950°-1,100°C. The conditions of reduction, such as temperature, time and hydrogen flow, have an important bearing on the particle size of powder produced, which, for most purposes, ranges as in the case of tungsten from 0.1 to 6 micron.

PRESSING

For the manufacture of rod, wire or sheet the powder is pressed into bars of sizes up to approximately 1 in. × 1 in. × 20 in. long for tungsten and 2 in. × 2 in. × 20 in. long for molybdenum in low alloy steel dies. Owing to this shape, die construction is simplified by using double action presses. The press illustrated in Fig. 2 has a horizontal ram for holding the assembled die containing the powder and a vertical ram for compacting the powder. Pressing pressures range from 15 to 25 tons/in.² These sizes are entirely adequate to meet the requirements of the lamp, valve and other industries.

However, the increased demand for larger pieces, with particular reference to molybdenum, has necessitated the introduction of hydraulic presses up to 3,000 tons capacity. Under applied pressure of about 20–25 tons/in.², it is now possible to press bars approximately 120–150 in.² in area with a press height of approximately 4 in., which corresponds to weights of 90–110 lb. The application of pressure, when pressing such bars is usually on one side only⁵. In addition, increasing use is being made of hydrostatic pressing using rubber bags. With this technique and using a pressure of 25 tons/in.² pressings weighing up to 400 lb. have been made⁶.



Courtesy of The General Electric Company Limited of England

Fig. 2. Hydraulic press.

Methods used in the production of ceramic products and techniques used in making hard metal dies from tungsten carbide–cobalt powder have been successfully adapted for use in fabricating molybdenum. For example, metal crucibles are formed by pouring a slurry of the powder into a plaster of Paris mould, then tilting the mould to drain off the residual liquid. The drained slip is air-dried and removed. In a second method, molybdenum is hot-pressed in a carbon mould heated by a high frequency induction furnace. Pressure used is approximately 0.25 tons/in.². A temperature of 1,500°C is necessary to obtain maximum density. The carbide skin is removed by heating in a hydrogen atmosphere at about 1,300°C for several hours⁷.

SINTERING

The demands made since approximately 1945 for parts having dimensions substantially greater than hitherto have forced manufacturers to produce much larger sintered bars. This has required larger sintering equipment and the development of alternative methods of sintering.

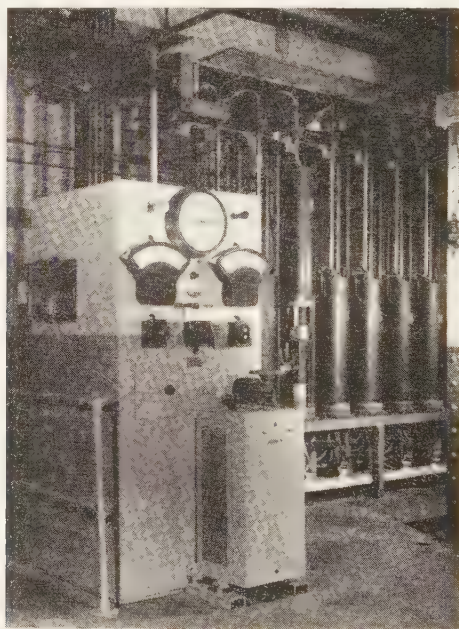
Direct sintering

The pressed bars, owing to their fragility, are heated to 1,100–1,300°C in a hydrogen atmosphere prior to sintering to facilitate handling.

Sintering is carried out in a vertical water-cooled copper bell-jar. The bar is held

at the top between a fixed pair of heavy water-cooled copper blocks faced with tungsten strips, and its lower end is attached either to a moveable tungsten or molybdenum clip immersed in mercury or to flexible contact terminals of molybdenum or tungsten, thus eliminating the mercury which is not favoured in some countries because of its toxic properties. After lowering the water-cooled copper bell-jar onto its base and replacing the air with oxygen-free dry hydrogen, an electric current, which for the larger bars is several thousand amperes at low voltage, is passed through the bar. The sintering temperature for tungsten and molybdenum is about $3,000^{\circ}$ and $2,400^{\circ}\text{C}$, respectively; the times range from 20 to 45 min. During sintering the tungsten bar contracts 16–18% with a corresponding increase in density from 11 to 18 g/cm³.

A typical sintering plant is shown in Fig. 3. This plant has twelve sintering jars, which are electrically connected in series with parallel feeds for cooling water and hydrogen. For continuous production it is convenient to control automatically the sintering process, thus ensuring that all material is subjected to the same heating schedule.



Courtesy of The General Electric Company Limited of England

Fig. 3. Plant for sintering tungsten and molybdenum.

Following the demand for large shaped pieces in recent years, manufacturers have been forced to produce larger sintered bars by the existing direct sintering method. Though it is possible to increase the length of the bar within limits which are imposed by the fragility of the pressed bar, the construction of the sintering jars, current supply, etc., serious difficulties are encountered when attempting to increase substantially the cross section. This is due to the fact that the temperature gradient

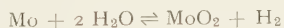
between the core and surface of the bar increases with increasing cross-section, resulting in either fusion at the core or an incompletely sintered surface. Today, bars of dimensions 2 in. $\times$ 2 in. $\times$ 40 in. long are sintered by direct current, and for this purpose large sintering bell-jars having a current consumption of up to 50,000 amperes are required^{5,8}.

The sintered bar sizes produced by the direct sintering method are adequate to meet the requirements of the lamp and valve industries, and the technique is universally practised today.

Indirect sintering

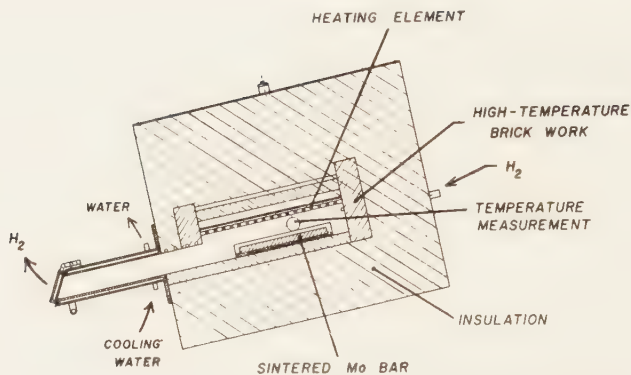
While the foregoing procedure was adequate for some purposes, it did not permit the production of molybdenum plate and sheet in sizes large enough to meet a demand which developed around 1945. Experimental work to overcome this difficulty was carried out by the Westinghouse Corporation, who modified the sintering method so that sintered and worked parts weighing up to several hundred pounds could be prepared. The method consists of sintering the compacted powder at considerably lower temperatures, 1,500–1,900°C, thus enabling the process to be carried out in molybdenum-wound furnaces of the static or pusher type. To achieve sintering at the lower temperatures, the pressed parts are exposed to a hydrogen atmosphere saturated with water vapour between 20–40°C.

The crystallisation induced by the presence of water vapour, which accelerates sintering of the molybdenum particles into dense ingots, takes place at quite low temperatures, 600–700°C, but much higher temperatures are required if sintering is to be completed in a short time. An interesting feature of this sintering technique is the use of a special support for the pressed molybdenum being sintered. When sintering large pressed parts of the order of 20–30 in. in length in molybdenum boats, there is a tendency for the compact to weld to the surface of the boat, this occurring before shrinkage (15–17%) is complete. This results in transverse cracks. To obviate this difficulty the pressed molybdenum parts are supported on thin corrugated molybdenum strips. The upper portions of the corrugations are coated with finely divided alumina or zirconia. The present technique is to heat the pressings in the reactive atmosphere at a temperature between 1,500–1,700°C for 2–3 h. Under these sintering conditions, the following oxidation-reduction reaction occurs between the metal and the hydrogen-water vapour



Density values up to 10 g/cm³ have been obtained as compared with the more usual 9.6–9.7 by the direct sintering technique. It is claimed that the application of heat externally instead of internally results in greater uniformity of heating, and as a result the final metal has a more uniform and smaller grain size than that obtained by direct sintering at a higher temperature. By this method, it is also possible to produce complex shapes by machining blanks after they have been given a preliminary heat treatment at about 1,100–1,300°C, which strengthens the blank without promoting any substantial degree of sintering^{9,10}.

A typical high-temperature muffle for sintering is shown diagrammatically in Fig. 4¹¹.



Courtesy of Metallwerk Plansee, Austria

Fig. 4. High-temperature muffle furnace for sintering molybdenum.

POWDER PROCESS FOR MELTING AND CASTING MOLYBDENUM

In 1943, R. M. PARKE AND J. L. HAM¹² of the Climax Molybdenum Co., developed a method of melting and casting molybdenum using an electric arc operating in vacuum. Initially the upper electrode was made up of a series of pressed and sintered bars joined together, the arc being struck between the vertical electrode and a lower liquid electrode which was supported in a water-cooled copper mould. To eliminate the necessity of using a consumable electrode PARKE AND HAM developed this process in which molybdenum castings are prepared direct from molybdenum powder.

The process consists¹⁰ of five distinct operations carried out *in vacuo*. These are coordinated to form automatically a molybdenum casting from powder. These operations are:

- (i) pressing the powder into a continuous rod,
- (ii) partially sintering the rod by electrical resistance heating,
- (iii) melting the end of the rod in an electric arc,
- (iv) deoxidising the molten molybdenum with the addition of carbon,
- (v) casting in a water-cooled copper mould.

The production of a continuous rod is obtained by a pelleting operation which presses each new pellet on top of its predecessor. The use of a collet type of mould instead of a simple cylinder overcomes difficulties associated with wall friction, etc. The collet also serves as one contact for introducing the sintering current, the second contact being a short distance below the collet. During the passage of the pressed rod from the collet to the second contact a sintering current of several hundred amperes is applied. The maximum temperature of the rod at this stage is 1,500°C. The partially sintered rod formed by this operation is strong enough to suspend itself from the contact, thus becoming a consumable electrode. So satisfactory has this technique proved itself that it is now capable of producing ingots up to 1,000 lb. in weight¹³.

LIQUID-PHASE SINTERING AND INFILTRATION TECHNIQUE

With the exception of certain specialised sintered products, it is desirable to approach as near as possible to the theoretical density in a sintered compact. In solid-phase sintering the rate of approach to theoretical density is often inconveniently slow, and

it is well-known that the presence of a liquid phase during sintering accelerates the rate of densification and facilitates the attainment of near-theoretical density. In the manufacture of alloys such as, for example, sintered Alnico, the liquid phase may be present for only part of the sintering period, but it aids alloying and densification. On the other hand, the liquid phase may be present throughout the period during which the compact is at sintering temperature. The well-known high density alloys based on tungsten are examples of sintered products produced in this way¹⁴. In addition, the well-known pseudo-alloys, for example, tungsten-copper and tungsten-silver are typical examples of the infiltration technique, in the application of which the pores of a pre-sintered tungsten body are saturated with either copper or silver by simply immersing part of the body in the metals whilst they are molten.

In considering the various methods used for sintering tungsten and molybdenum, it is possible that the application of these techniques may be of interest. Using these techniques, the sintering temperature is considerably lowered and the material in the sintered condition is readily machined. It is of interest to note that sintered parts of tungsten base high density alloys weighing up to 500 lb. have been produced. Though alloys of this type generally contain 5-15% of elements substantially lower in melting point than tungsten¹⁵, near theoretical density can be achieved by the addition of, for example, as little as 0.25% nickel to tungsten^{16,17}.

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THE EFFECT OF ROLLING TEMPERATURE ON THE MECHANICAL PROPERTIES OF MOLYBDENUM

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SUMMARY

The effect of initial breakdown at 1,350°C or 1,000°C and final rolling at 1,000°C, 800°C, 600°C or 400°C on the mechanical properties of arc-melted molybdenum is shown. Tensile, impact and slow bend test results are presented and the influence of stress relief and recrystallisation is also illustrated. The bearing of these results on the production and properties of strip and sheet is discussed.

INTRODUCTION

The aim of the work was to establish what factors are important in processing of arc-cast molybdenum, and to what extent they influence the tensile strength and ductile/brittle transition temperature.

MATERIAL

Two-inch diameter ingots of the compositions indicated in Table I were produced by arc-melting 10 mm diameter sintered rods in vacuum, using carbon as deoxidiser. The burn-off rate was about 10 g/sec and the arc current about 1,200 A d.c., with the electrode negative. The ingots were turned to 1½ inch diameter and rolled through grooved rolls to 1-inch square bars, either at 1,000°C or 1,350°C, with reheats, as necessary, in a hydrogen atmosphere furnace.

The 1-inch bars were annealed at 1,350°C for 1 hour in hydrogen to relieve stresses and to allow recrystallisation to occur. They were then flat-rolled at various temperatures between 400°C and 1,350°C to produce strip approximately ¼ in. thick and 1½ in. wide. A few bars were rolled using 10% reduction in thickness per pass, but the greater part were given four passes of 30%. Full details of rolling are given in Table I.

All specimens were cut perpendicular to the rolling direction. For tensile tests a Hounsfield No. 11 specimen was used; for impact transition determinations a sub-standard V-notch Charpy (5 × 5 × 30 mm, notch 1.5 mm deep, 0.25 mm root radius) was used and for bend transition determinations an ½ in. diameter by 1-in. long specimen. The Charpy specimens were notched on a face perpendicular to the rolling direction.

TABLE I

Analysis % C	Rolling temperature, °C		Pass reduction in final rolling	Final state
	Initial	Final		
0.0087	1350	400	30%	As-rolled
0.0086	1350	400	30%	Recrystallised
0.010	1350	600	30%	As-rolled
0.0062	1350	600	30%	Recrystallised
0.013	1350	800	30%	As-rolled
0.0052	1350	800	30%	Recrystallised
0.0062	1350	1000	10%	As-rolled
0.0062	1350	1000	30%	As-rolled
0.0049	1350	1000	30%	Recrystallised
0.0074	1350	1350	10%	As-rolled
0.0074	1350	1350	30%	As-rolled
0.002	1000	400	30%	As-rolled
0.002	1000	400	30%	Recrystallised
0.014	1000	600	30%	As-rolled
0.014	1000	600	30%	Recrystallised
0.0085	1000	850	30%	As-rolled
0.0085	1000	850	30%	Recrystallised
0.0096	1000	1000	30%	As-rolled
0.0096	1000	1000	30%	Recrystallised

All bars were annealed at 1,350°C for 1 h before final flat rolling. The recrystallising treatment was 1 h at 1,300°C.

Impurities common to all materials (approx.)

Element	Al	Co	Cr	Cu	Fe	Ni	Si	Ti	W	O ₂	N ₂
Weight%	< 0.005	0.01	0.003	0.005	0.005	0.005	0.002	0.028	< 0.01	< 2 p.p.m.	< 2 p.p.m.

TESTING METHODS

Tensile tests were carried out on a Hounsfield Tensometer at a cross head traverse rate of 0.0095 in./min, corresponding to a plastic strain rate of 0.00033 sec⁻¹ approximately. For low temperatures a cooling bath of acetone and solid carbon dioxide was used.

Bend test specimens were bent in a jig over a $\frac{1}{4}$ in. diameter former at a rate of traverse of 0.0075 in./min, corresponding to an initial strain rate of about $1.1 \cdot 10^{-4}$ sec⁻¹ in the outer fibres. Low temperatures were obtained by passing air cooled in liquid nitrogen through the apparatus.

Impact tests were made on a bench machine having an energy of 10 ft. lb.

The temperatures were controlled to $\pm 1^\circ\text{C}$ during the tensile and bend tests, and to $\pm 5^\circ\text{C}$ for the impact tests.

TENSILE PROPERTIES

The tensile properties are shown in Fig. 1. The maximum stress increases significantly with decreasing rolling temperature in the case of material initially rolled at 1,350°C, reaching a maximum for a final rolling temperature of 600°C. The ductility, as measured by elongation, is relatively unaffected by the rolling temperature. The anomalously high elongation of the 400°C specimen when tested at -10°C is not understood; there was no apparent peculiarity in the specimen itself. The maximum stress

of material initially rolled at 1,000°C is much less dependent on the final rolling temperature, and does not attain such a high value as it does when initially rolled at 1,350°C. When the final rolling temperature is 1,000°C, the maximum stress is significantly higher than that of the material initially rolled at 1,350°C, but decreasing the rolling temperature has little further effect. Specimens of the series initially

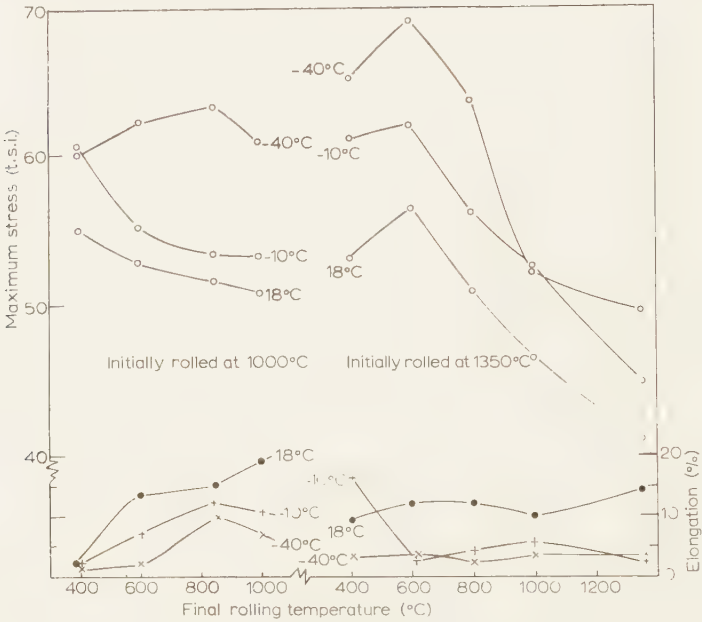


Fig. 1. Tensile strength and ductility of as-rolled molybdenum, showing variation with rolling temperature.

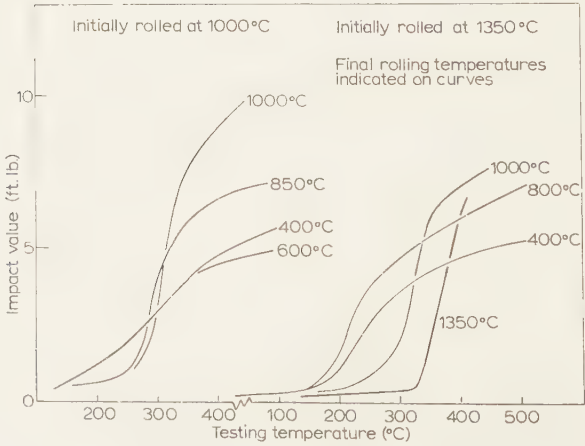


Fig. 2. Effect of rolling temperature on V-notch impact transition temperature of as-rolled molybdenum.

rolled at $1,000^{\circ}\text{C}$ tended to fracture in a manner indicative of the presence of micro-cracks in a plane parallel with the plane of flat rolling. This effect was very pronounced in the material finally rolled at 400°C , and present to some degree in all but a few of the specimens. The elongation results are somewhat erratic, but they are in general greater than for material initially rolled at $1,350^{\circ}\text{C}$.

The above paragraph refers to material initially rolled in grooved rolls and finally flat-rolled with 30% reduction per pass. A limited study was also made of the effects of forging the ingots to a rough square section prior to groove rolling at $1,350^{\circ}\text{C}$ and of the effect of 10% reductions in the final flat rolling at $1,000^{\circ}\text{C}$ and $1,350^{\circ}\text{C}$. The general conclusion was that initial forging gave slightly improved ductility in the rolled strip, but that the effect was not sufficiently striking or consistent to justify a full study. Similarly, no significant differences were observed when comparing 10% and 30% reductions.

IMPACT TRANSITION TEMPERATURE

Curves of energy absorbed *vs.* testing temperature are shown in Fig. 2 for the different rolling temperatures. For material initially rolled at $1,350^{\circ}\text{C}$ the impact properties are very dependent on the final rolling temperature, but for material initially rolled at $1,000^{\circ}\text{C}$ the transition temperature is virtually independent of the final rolling temperature. The maximum energy which can be absorbed, at a temperature slightly above the transition, is greater for the higher final rolling temperatures in both series of tests.

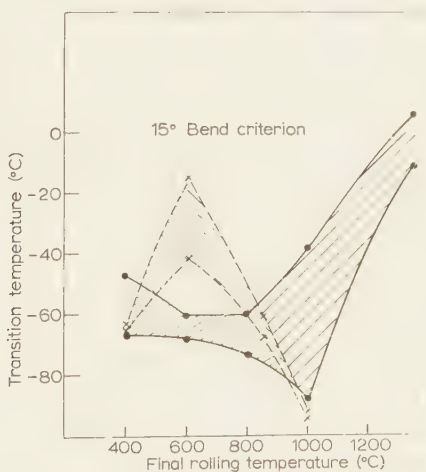


Fig. 3. Variation of slow-bend transition temperature with rolling temperature. $\times$ --- $\times$ Initially rolled $1,000^{\circ}\text{C}$; $\bullet$ — $\bullet$ initially rolled $1,350^{\circ}\text{C}$.

BEND TRANSITION TEMPERATURE

For many treatments graphs of bend angle *vs.* temperature show large scatter of results. This is shown in Fig. 3, which gives the best and worst transition temperatures based on a 15 degree bend criterion, corresponding to approximately 2% strain in the outer fibres of the specimen. In the material initially rolled at $1,350^{\circ}\text{C}$, it is obvious that there is a considerable reduction in transition temperature when final

working is done below the recrystallisation temperature. It is of interest to note that the largest scatter in results is obtained at 1,000°C, which is only just below the recrystallisation temperature. However, this effect does not arise in the material initially rolled at 1,000°C, where uniform results are obtained. The high transition temperature and large scatter of the 600°C material is believed to arise from micro-cracks produced in rolling (*c.f.* low impact values and tensile strengths).

EFFECT OF HEAT TREATMENT

Strip rolled at various temperatures has been tested in a fully recrystallised condition. The tensile results are shown in Fig. 4. Fairly uniform properties are obtained where initial rolling has been carried out at 1,000°C, and the variations in tensile

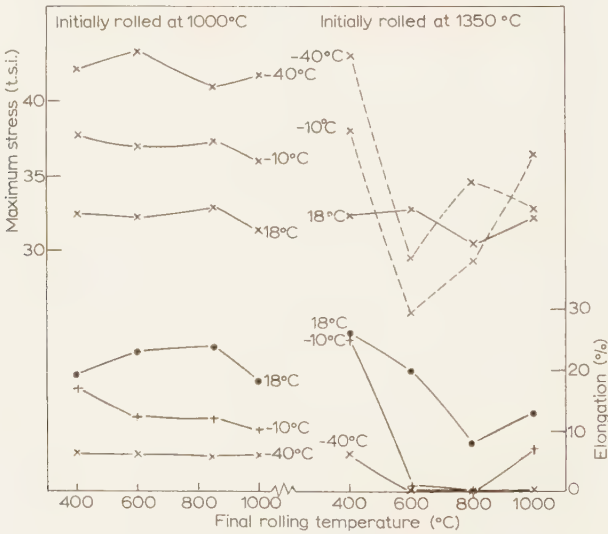


Fig. 4. Tensile strength and elongation of fully recrystallised molybdenum for various rolling temperatures.

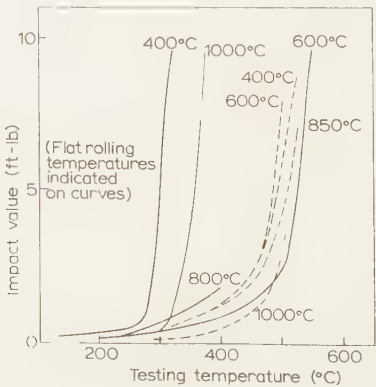


Fig. 5. V-notch Charpy transition curves for fully recrystallised molybdenum, showing the effects of rolling temperature. Initial rolling at ——— 1,350°C, - - - - - 1,000°C.

strength and ductility with the final rolling temperature are not significant. When the initial rolling temperature was $1,350^{\circ}\text{C}$, the properties are not generally as good as for the material initially rolled at $1,000^{\circ}\text{C}$, with the exception of the strip finally rolled at 400°C , which is considerably better. The poor results of the material rolled at 600°C and 800°C are probably due to variation in ingot quality rather than to final rolling temperature. (The ingots used for these tests are different from those used for the as-rolled investigations.)

The notched Charpy tests (Fig. 5) results follow the same pattern. There is no significant difference in the transition temperature (approx. 500°C) of material initially rolled at $1,000^{\circ}\text{C}$, but for the material initially rolled at $1,350^{\circ}\text{C}$, the strip finally rolled at 400°C and $1,000^{\circ}\text{C}$ has much lower transition temperature (280°C and 330°C).

The slow bend transition temperatures based on a 15 degree criterion vary randomly between -30°C and -60°C in both cases. There is no apparent dependence on final rolling temperatures, but the higher initial rolling temperature gives the more scattered results.

Some additional work has been carried out on the variation of the tensile properties with annealing temperature. Miniature specimens (diam. 0.075 in., gauge length 0.5 in.) were tested at room temperature on a photographically recording Chevenard apparatus, which had been modified to provide for axial straining of the specimen at a stress head travel rate of 0.0062 in./min, corresponding to a plastic strain rate of 0.00024 sec^{-1} . Transverse specimens were machined from $\frac{1}{4}$ in. thick molybdenum strip (containing 0.047% carbon) which had been flat rolled at 600°C . These were annealed for one hour at various temperatures and subsequently electropolished. One hour treatments at 900°C , $1,100^{\circ}\text{C}$, $1,200^{\circ}\text{C}$ and $1,400^{\circ}\text{C}$ were carried out in hydrogen, and those at $1,800^{\circ}\text{C}$ and $2,200^{\circ}\text{C}$ in a tungsten tube furnace *in vacuo* ($0.1\text{ }\mu$). Specimens were removed from the hot zone and cooled in hydrogen or *vacuo* respectively.

The results are shown in Fig. 6, and typical load-extension curves in Fig. 7. There is no yield point either in the as-rolled condition or after annealing at 900°C . There

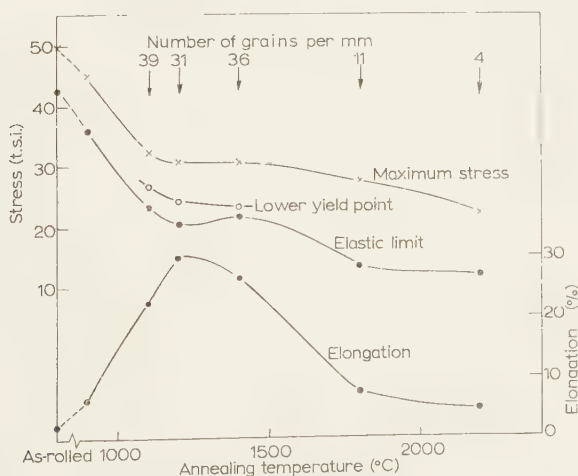


Fig. 6. Tensile properties of Mo-0.047%C at 20°C , after annealing for 1 h at various temperatures.

is a slight yield point after annealing at $1,100^{\circ}\text{C}$ and a large one after treatments at $1,200^{\circ}\text{C}$ and $1,400^{\circ}\text{C}$. The stress-strain curves for the treatments at $1,800^{\circ}\text{C}$ and $2,200^{\circ}\text{C}$ have continuous curvature, very similar to the curve obtained from the as-cast material. The maximum elongation for this series is obtained at $1,200^{\circ}\text{C}$ which corresponds approximately to the lowest temperature for complete recrystallisation.

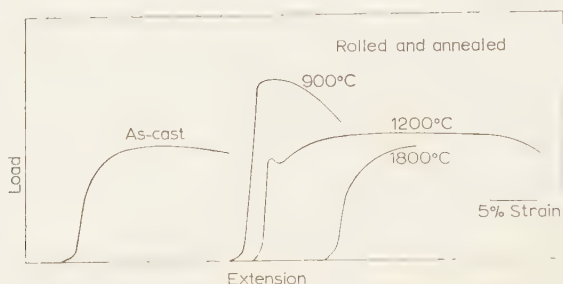


Fig. 7. Typical Chevenard traces for Mo-0.047% C in various conditions.

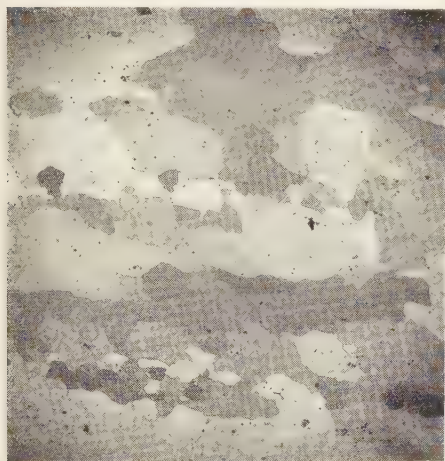
The recrystallised grain sizes are shown in Fig. 6, and were determined by the linear intercept method on a transverse section of the shoulder of the specimens; unrecrystallised areas were ignored. Considerable grain growth has occurred at the higher annealing temperatures, and a decrease in elastic limit is to be expected from the Petch relationship between yield stress and grain size. More recent experiments on a Mo-0.01% C material have shown that the cooling rate has an important effect. Specimens rapidly cooled from $1,800^{\circ}\text{C}$ have given distinct yield points and good elongations (approx. 25%) while slightly slower cooling (similar to that of the $1,800^{\circ}\text{C}$ and $2,200^{\circ}\text{C}$ specimens in Fig. 6) has resulted in no yield point and an elongation of only 5%. There is also a significant difference in yield stress (approx. 4 tons per square inch) for the specimens cooled at these two rates.

DISCUSSION

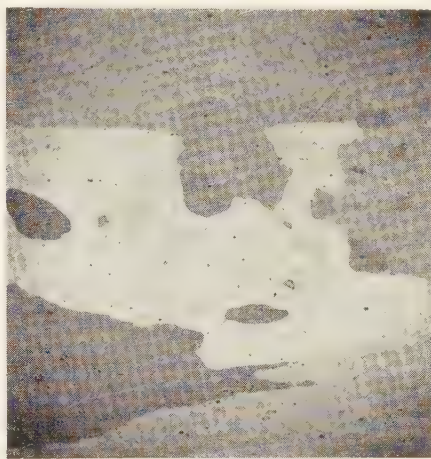
There is no significant variation in the properties of finally recrystallised molybdenum with the various working schedules, so it is only necessary to consider the as-rolled properties. The conclusion to be drawn is that when initial rolling has been at $1,350^{\circ}\text{C}$, it is best to carry out final rolling at a temperature below $1,000^{\circ}\text{C}$. There is a distinct improvement in tensile strength down to a rolling temperature of 600°C without any loss of ductility, and also a reduction in impact and bend transition temperatures. When initial rolling has been at $1,000^{\circ}\text{C}$, these findings do not apply: it is then best to roll finally at $1,000^{\circ}\text{C}$, for while the impact transition temperature varies little with final rolling temperature, the bend transition temperature is lowest for rolling at $1,000^{\circ}\text{C}$, and the highest impact value also occurs in this case. In addition, many of the Hounsfield specimens from material rolled at 400°C and 600°C were found to have cracks. The choice of initial rolling temperature depends upon which property of the finished strip is of interest. If tensile ductility is the main criterion, then the initial rolling temperature of $1,000^{\circ}\text{C}$ is preferable, with final rolling at 850°C or $1,000^{\circ}\text{C}$. If a high tensile strength is required, then it is necessary to work initially at $1,350^{\circ}\text{C}$ and finally

at 600°C; lowest impact transition temperatures are obtained by initial rolling at 1,350°C and final rolling at 400°C or 800°C.

The differing results from the specimens rolled at 1,000°C and at 1,350°C are considered to arise from the different microstructures of the 1-in. square bars after the anneal at 1,350°C (Fig. 8a and b). In the bars rolled at 1,350°C, insufficient stress is built up to enable appreciable recrystallisation to occur on annealing at 1,350°C. The grains are large and irregular and many contain well developed substructure. In the bars initially rolled at 1,000°C there is almost complete recrystallisation after annealing at 1,350°C and the resulting grain size is small. The large grain, stress-relieved material is capable of more work hardening than the small grain, recrystallised material but exhibits lower ductility in the worked condition. This may be because the stress-relieved material contains many more obstacles to slip in the form of polygon boundaries than the recrystallised material.



a



b

Fig. 8. Microstructures of 1-in. square bars annealed at 1,350°C for 1 h after initial rolling at (a) 1,000°C (b) 1,350°C. ($\times 42$)

The relation of the properties of thin strip and sheet (down to 0.020 in.) to this method of manufacture is an interesting illustration of the significance of the results reported for thicker material. Quantitative figures will not be quoted since much of the testing was of a simple bend test type designed to enable the material to be evaluated from a practical "workshop" aspect. The most important property in thin sheet or thin strip was considered to be the ability to withstand reasonable deformation in bending of the type commonly used in fabrication. Such material rolled from arc-cast molybdenum-carbon ingots was found to give the best combination of strength and ductility if the rolling temperature did not exceed 1,000°C and was not allowed to fall below 800°C except in the very thinnest gauges. It will be noted from Fig. 1 that the most consistently high elongation results at room temperature are obtained by rolling in this range of temperature. The elongation in tension would, of course, be expected to correlate with bend test criteria.

Since we are here dealing with material which has been reduced as much as 98%,

by cold rolling, it is to be expected that the resulting product would become brittle if any lower temperature were used, and this was found to be the case. However, in the temperature range used for the best type of product, the material is being rolled (always with reheating of about 1 minute between passes) in the region where stress relief can take place, thus enabling rolling to continue. In these conditions the hardness does not rise much above VPN 270. On the other hand, experience with thin sheet and strip from arc-cast molybdenum has confirmed what has been known for many years to the industry dealing with the sintered material, namely, that if at any stage the metal is allowed to recrystallise, then an apparent brittleness results and fracture is very liable to occur on the next pass through the rolls. This apparent brittleness is obviously the same as the apparent brittleness which has long been known to occur in sheet and wire when recrystallised. The phenomenon is also well known in the tungsten industry. The term "apparent brittleness" is used because the effect can now be understood in the light of results recorded in this paper. Molybdenum is quite highly sensitive to rate of deformation, it is affected by triaxiality of stress and shows a marked transition temperature.

Whether a piece of molybdenum sheet fractures in rolling or workshop handling depends almost entirely on whether the conditions of rate, stress concentration and temperature are such that the material is above or below its transition range. The transition temperature, however it is measured, is always quite sharp for recrystallised material, while as the amount of cold work is increased the transition extends over an increasing range of temperature. This effect is obvious even in the limited set of results given in Fig. 2.

Bend test results on thin sheet and strip show that most ordinary bends made at room temperatures without heating and at normal rates of bending are actually occurring in the range where recrystallised material is below its transition temperature and consequently appear quite brittle. Heavily cold worked material, however, though below its upper transition point, has not yet reached the fully brittle condition and in consequence is relatively easy to work.

DEVELOPMENT OF REFRACTORY METAL SHEET IN THE UNITED STATES

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SUMMARY

The new airframe applications for refractory metals in aircrafts, missiles, and space vehicles will require primarily sheet. Development of high quality sheet products and components of the four major refractory metals is being accelerated in the United States. Emphasis is being placed on relatively thin gauge sheet of normal sizes, but with exceptional surface quality and gauge control. Strength appears secondary to fabricability and quality. United States industry is very active in the development of refractory metals and is introducing special mill equipment for their processing. A coordinated refractory metal sheet-rolling programme has been organized to develop methods for producing advanced refractory metal alloys in sheet form and to provide production quantities of sheet for development of design criteria data and for fabricating, joining, and coating components of interest in the new applications.

Refractory metals have been under development for a great many years in the United States. For the most part, however, the refractory metals were not developed to the point that they could be considered for use for massive, structural applications. Recognizing that this situation might indeed change, programmes were initiated by the United States Government after World War II to provide a technical basis for selecting advanced alloys and bringing them to the state of production availability necessary for their use in structures.

Extensive programmes were conducted on the metallurgy of molybdenum. More recently, a series of programmes were initiated on columbium, and still more recently on tungsten and tantalum. It is the purpose of this paper to describe technically the status of development of sheet alloys of these materials from the standpoint of the users and the producers. The paper will also discuss one large programme now in progress to support the more rapid development of high-quality refractory metals sheet, the so-called Refractory Metals Sheet Rolling Programme.

The airframe industry and the rocket motor industry constitute the users of refractory metals at the present time. Re-entry glide vehicles are currently being designed to operate under conditions for which refractory metals are required. Sheet products are applied to the leading edge sections, and to the positions back on the underside of the lifting surface, and the vector controls. Rocket nozzles are also being fabricated from refractory metals. Ramjet motors for operation above Mach 3, and some sections of the turbojet engines operating above Mach 3, also require refractory metals. The most difficult mill product to make at the present time is sheet, though billets and forged parts cannot be considered to be simple production items.

Most advanced applications of refractory metals favour the use of sheet although machined forgings are already in use for rocket nozzles. The gauges for structural application range from 0.010–0.100 in., *e.g.*, the same as the range for low-temperature airframe construction. Sheet sizes of interest also are conventional, up to 36 in. $\times$ 96 in., with the potential users willing to accept somewhat smaller sizes if necessary. Quality requirements are high and gauge tolerances must be somewhat better than $\pm 10\%$, because of the drastic weight penalties which would result from surplus material because of the high density of the refractory metals.



(Courtesy Boeing Airplane Company)

Fig. 1. Simulated leading edge constructed from molybdenum–0.5 titanium using rivetted construction.

There are two schools of thought with respect to the use of refractory metals in leading surfaces. One school of thought, the “hot structure” school, believes that the refractory metal should support the aerodynamic and thermal stresses developed during re-entry. The other school of thought believes that the function of refractory metal should be as a heat shield, backed by insulation and in order to permit the use of an efficient, low-temperature structural member. The design stresses expected for either application are not high, but in the hot structure design, use could be made of improved strength at elevated temperatures. Strength is not a significant

factor in the heat shield design, but methods of attachment of the skin to the insulation must be solved. This may necessitate a modest strength requirement.

Methods of construction of hot structures include conventional sheet and stringer such as shown in Fig. 1. Corrugated sandwich construction is being considered for many of the skins. Weldability is very desirable as a weight-saving measure, although not mandatory, particularly in view of the thermal stresses that may make it impracticable to have large, continuous structure.

The temperatures expected for hot-structure design range from about 2,000 to 4,000°F depending on the trajectory during re-entry. Small errors in the re-entry angle of inclination will cause large increases in temperature. Therefore, temperatures up to 4,000°F are possible in some designs. In the heat shield application, the refractory metal shield also may assume the full equilibrium temperature, and could develop 4,000°F or perhaps more. Coating systems to protect against oxidation and other corrosive environments may well prove to be the limiting factor in the use of these refractory metals, since strength requirements are quite modest and well within the existing state of the art. Another factor of importance is emissivity of the exposed surface, either the coating or, if oxidation-resistant, the refractory metal itself. Emissivity should be at least 0.8 or above to provide efficient radiative cooling.

Efforts to develop refractory metals in the United States have been very active in the past few years. Molybdenum is furthest along in development, but the rate of progress on columbium is so fast that it is expected to catch up with molybdenum within the next several years. However, economic factors probably will weigh in favour of molybdenum for somewhat longer. The competition between molybdenum and columbium for the leading edge application is very spirited. The advantages of one are offset by those of the other. Columbium has been considered to have the advantage of low-temperature ductility and weldability. However, the alloys of columbium that have high-temperature strength approaching that of molybdenum generally lose much of the fabricability and ductility of pure columbium. Accordingly, the properties of each of the alloys must be examined carefully in drawing a proper comparison between these two alloy-base materials. Tungsten and tantalum are not competitive with lower-density molybdenum and columbium as sheet for the lower leading edge temperatures now of major consideration, and activity is directed toward their use as forgings for solid-propellant rocket motors or for sheet applications in rocket motors, such as flame shields in jetevators or flame skirts in liquid-propellant rockets. At the present time these are relatively minor problems compared to the nozzle itself. For leading edge applications, below 2,500°F molybdenum and columbium are the favoured materials. Above 2,500°F, sheet tungsten and tantalum alloys are considered most suitable. Because of tantalum's superior sheet producibility and low-temperature ductility, it is probably the leading candidate for leading edge use above 2,500°F.

In a recent survey of refractory metal producers, it was found that the following distribution of interest existed:

Molybdenum	6 companies
Columbium	8 companies
Tantalum	4 companies
Tungsten	4 companies

The compositions and consolidation method of some of the alloys are listed below:

<i>Alloy composition (wt. %)</i>	<i>Consolidation method</i>
Molybdenum	
0.5 Ti	Arc-cast
0.5 Ti-0.07 Zr	Arc-cast
0.05 Zr	Arc-cast
1.25 Ti-0.15 Zr-0.15 C (TZC)	Arc-cast
0.5 Zr	Arc-cast
0.5 TiO ₂	Powder met.
Columbium	
15 W-5 Mo-1 Zr-0.05 C (F 48)	Arc-cast
15 W-5 Mo-1 Zr-5 Ti-0.05 C (F 50)	Arc-cast
1 Zr	Arc-cast
10 Mo-10 Ti (D 31)	Arc-cast
20 W-10 Ti - 6 Mo (D 41)	Arc-cast
15 W- 20 Ta	E. B. Melt
20 W-20 Ta	E. B. Melt
33 Ta-1 Zr (FS 82)	Arc-cast
Tantalum	
10 W	Arc-cast
Tungsten	
2 ThO ₂	Powder met.

Sheet capabilities vary considerably depending on the status of the product being rolled. Refractory metal producers have been able to fabricate the unalloyed metals, except for tungsten, in 36- by 96-in. sheets in gauges down to 0.040 in., although the sheets sometimes are short of desired quality. Tungsten sheets are limited by the size of the sheet bar and furnace equipment used, and are rolled in sizes such as 20 × 36 × 0.080 in. Sheets 24-in. wide can probably be rolled down to about 0.02 in., but for thinner gauges the width must be less.

Refractory metal sheet is fabricated in conventional equipment at the present time. Because refractory metals are characterized by the excellent retention of strength to high temperature, rather than by very high strength levels, the flow stresses for fabrication are not too high for conventional equipment. However, a general problem is constituted by the inadequate furnaces for preheating sheet bar and sheet prior to rolling. Much production equipment consists of gas-fired furnaces with a maximum temperature capability of 2,400°F. Many U.S. refractory metal producers are installing new furnace equipment intended expressly for refractory metal processing. As an example, the du Pont Company, Metal Products Division, is setting up a refractory metal conversion facility in Baltimore, Maryland. As another example, the U.S. Navy facility recently constructed at the Universal-Cyclops Company at Bridgeville, Pennsylvania, under a contract with the Bureau of Naval Weapons includes two 4,000°F furnaces with a maximum capacity of 16 in. wide, 10 ft. long, and induction heating

coils for billet heating capable of 12-in. diameter, 40 in. long. The furnaces will be operated in an argon-filled room, 80 ft. by 40 ft. and 20 ft. high.

The producers of powder-metallurgy material generally have hydrostatic chambers for compaction of billets up to 12 in.-diameter, 36 in. long. Pressures usually are about 30,000 p.s.i. but in some cases extend to 100,000 p.s.i. Sintering furnaces for hydrostatically pressed billets are generally of the resistance type, capable of 3,500 to 3,600°F. Some producers use induction sintering.

Many refractory metal producers are installing new mill equipment. Du Pont is setting up a versatile mill facility in Baltimore. Refractory metal mills are also being set up by Wah Chang in Albany, Oregon; Sylvania in Towanda, Pennsylvania; and Universal-Cyclops in Bridgeville, Pennsylvania.

The need to control surface contamination and maintain tight gauge control and high quality in refractory metals indicates that these special mills should be particularly useful. Universal-Cyclops' Infab rolling facility, mentioned above, is contained in the inert atmosphere room with other facilities for handling refractory metals, including forging, welding, and furnaces. Most of the equipment will be controlled remotely from the outside, but observers with respiratory equipment will be stationed in the room for observation and corrective action if necessary.

Most mill experience in fabrication of refractory metal sheet has been obtained on molybdenum and its alloys. A number of quality deficiencies have been observed, including surface contamination, brittleness along planes 45° and the rolling direction, variability in mechanical properties, high ductile-brittle transition temperature, lamination tendency, poor gauge control, poor flatness, low recrystallization temperature relative to that obtainable in barstock. Considerable progress has been made toward elimination of these difficulties in unalloyed molybdenum and the Mo-0.5% Ti alloy. However, experience with sheet production of the more advanced molybdenum alloys has been negligible. Sheet development of the strong alloys of columbium, tantalum, and tungsten has been much less than with molybdenum. Production of columbium alloy sheet for evaluation programmes has been slow, and often the product is not of the quality required by the users. Progress has been made rolling sheet of the more fabricable columbium alloys, such as Cb-10 Mo-10 Ti and Cb-33 Ta-1 Zr; the more difficult alloys, such as F 48, require considerably more development work.

Because of the above deficiencies and the need for an integrated approach, as well as support of volume operations, refractory metal sheet rolling programmes have been set up. A major programme has been initiated by the U.S. Navy Bureau of Naval Weapons. In this programme, the concept used in its previous programme for developing titanium sheet for the Department of Defense has been adopted with the extensive assistance of the Materials Advisory Board of the National Academy of Sciences. In the current programme, an advisory Refractory Metals Sheet Rolling Panel has been established, comprised of members representing producers, users, research organizations, and Government agencies. Important facets of the programme relate to the need to establish requirements for immediate (3 to 5 years) and more distant (5 to 10 years) periods, technical requirements and selection, coatings, quality specifications, standardization of test methods, and chemical analysis. A number of programmes involving molybdenum and tungsten alloys have been established and others are being initiated. The Alloy Requirements and Selection Group has set up ground rules whereby refractory metal alloys may be qualified for consideration for

production-development support. Since the refractory metal alloys are often not highly advanced, pilot as well as preproduction status was recognized. The following billet and sheet sizes were to have been produced in order to qualify:

1. *Pilot Development Status*

Ingots or billets: 2 in. minimum section

Sheet: 6 × 20 in. minimum size

2. *Preproduction Development Status*

Ingots or billets: 6 in. minimum section

Sheet: 18 × 48 in. minimum size

In order to include current electron-beam melting facilities for columbium or tantalum alloys, where the maximum ingot size is 5-in. diameter, the Ground Rules were relaxed to 5-in. section ingots and 12 by 36-in. sheets corresponding to preproduction status. Recognizing the difficulty of producing large tungsten sheets, sizes of 6 × 20 in. were taken as corresponding to preproduction as well as pilot status.

TABLE I
TARGET PROPERTIES FOR SELECTION OF MOLYBDENUM SHEET ALLOYS

	Fabricable molybdenum		High-strength molybdenum	
	In optimum condition	Compl. recryst.	In optimum condition	Compl. recryst.
Room temp. tensile				
Ultimate tensile strength, k.s.i.	*	*	*	*
Yield strength, 0.2% offset, k.s.i.	*	*	*	*
Elongation (%)	10	10	2	2
	In optimum condition		In optimum condition	
Elevated temp. tensile				
Temp. (°F)	2,000	2,400	2,400	3,000
Ultimate tensile strength, k.s.i.	75	50	75	25
Yield strength, 0.2% offset, k.s.i.	60	35	60	15
Elongation (%)	*	*	*	*
Creep rupture (State stress and elongation) at				
Temp. (°F)	2,000	2,400	2,400	3,000
Rupture-time (hours)	1 10	1 10	1 10	1 10
Recrystallization (In optimum condition) 50% by met. obs.				
Time (hours)		1		1
Temp. (°F)		2,600		3,200
Notch sensitivity - ratio**	1.0 (RT)		1.0 (200°F)	
Transition temp. (In optimum condition) in bending 4 T	-40°F		RT	
tensile, notched	State		State	
smooth	State		State	
Impact, Charpy	State		State	
Bend ductility (room temp.)				
Base metal	1 T		4 T	
Welded (Weld transverse to bend axis)	4 T		State	

* To be furnished

** K_t 6.0, RA 40% (See *ASTM Bull.*, Jan. (1960) 29)

The requirements for refractory metals sheet cover a wide range of mechanical properties. In some cases, producibility of wide, thin-gauge, high-quality sheet, capable of ductile welds, is more important than ultra high strength at elevated temperatures. In other cases, the ultimate in strength and recrystallization characteristics are needed and are considered more important than fabricability and quality aspects. These considerations were taken into account in the Refractory Metal Sheet Rolling Programme by setting up two classes of sheet products of molybdenum and columbium alloys; *i.e.* fabricable alloys and high-strength alloys. Temperatures of interest for the fabricable alloys range from 2,000 to 2,400°F, whereas the high-strength alloys are intended for use at somewhat higher temperatures.

Tungsten is perhaps the only unalloyed refractory metal where a sheet rolling programme may be justified. There is relatively little interest in unalloyed molybdenum, columbium, or tantalum for hot-structure applications. The fabricability of these metals when unalloyed offers few technical problems. If they are needed for heat

TABLE II
TARGET PROPERTIES FOR SELECTION OF COLUMBIUM SHEET ALLOYS

	Fabricable columbium		High-strength columbium	
	In optimum condition	Compl. recryst.	In optimum condition	Compl. recryst.
Room temp. tensile				
Ultimate tensile strength, k.s.i.	*	*	*	*
Yield strength, 0.2% offset, k.s.i.	*	*	*	*
Elongation (%)	15	15	10	10
	In optimum condition		In optimum condition	
Elevated temp. tensile				
Temp. (°F)	2,000	2,400	2,200	2,600
Ultimate tensile strength, k.s.i.	50	20	50	25
Yield strength, 0.2% offset, k.s.i.	40	15	40	15
Elongation (%)	*	*	*	*
Creep rupture (State stress and elongation) at				
Temp. (°F)	2,000	2,400	2,200	2,600
Rupture-time (hours)	1 10	1 10	1 10	1 10
Recrystallization (In optimum condition) 50% by met. obs.				
Time (hours)	1		1	
Temp. (°F)	2,400		2,800	
Notch sensitivity - ratio**	1.1 (RT)		1.0 (RT)	
Transition temp. (In optimum condition) in bending 4 T	-100°F		-40°F	
tensile, notched	State		State	
smooth	State		State	
Impact, Charpy	State		State	
Bend ductility (room temp.)				
Base metal	1 T		4 T	
Welded (Weld transverse to bend axis)	2 T		6 T	

* To be furnished

** K_t 6.0, RA 40% (See *ASTM Bull.*, Jan. (1960) 29)

TABLE III
TARGETS FOR SELECTION OF TUNGSTEN AND TANTALUM ALLOYS

	Unalloyed or dilute tungsten			High strength tungsten			Tantalum		
	In optimum condition	Compl. recryst.	In optimum condition	In optimum condition	Compl. recryst.	In optimum condition	In optimum condition	Compl. recryst.	
Room temp. tensile									
Ultimate tensile strength, k.s.i.	*	*	*	*	*	*	*	*	
Yield strength, 0.2% offset, k.s.i.	*	*	*	*	*	*	*	*	
Elongation (%)	2	*	2	2	*	15	15	15	
	In optimum condition			In optimum condition			In optimum condition		
Elevated temp. tensile									
Temp. (°F)	3,000	3,500	3,08	3,500	4,000	2,400	3,000	3,500	
Ultimate tensile strength, k.s.i.	20	10	36	27	15	35	25	15	
Yield strength, 0.2% offset, k.s.i.	15	7	24	18	10	28	16	10	
Elongation (%)	*	*	*	*	*	*	*	*	
Creep rupture (State stress and elongation) at									
Temp. (°F)	3,000	3,500	3,000		3,500	2,400	3,000		
Rupture-time (hours)	1	1	1	1	10	1	10	10	
Recrystallization (In optimum condition) 50% by met. obs.									
Time (hours)									
Temp. (°F)									
Notch sensitivity - ratio**									
Transition temp. (In optimum condition) in bending 4 T									
tensile, notched smooth									
Impact, Charpy									
Bend ductility (room temp.)									
Base metal									
Welded (Weld transverse to band axis)									

* To be furnished

** K_t 6.0, RA 40% (See ASTM Bull., Jan. (1960) 29)

shield applications, there would be little problem in obtaining large, thin-gauge sheets of excellent quality. High-strength tungsten alloys chiefly are of the nonmetallic dispersion type, exemplified by W-2% ThO₂. A characteristic of such alloys is that fabricability and low-temperature ductility is not diminished, while strength at elevated temperatures, particularly creep resistance, is greatly enhanced.

Although much less is known about tantalum alloys, it appears from the experience with Ta-10 W and from alloy development studies, that the fabricability and low-temperature ductility of these alloys is outstanding. Tantalum alloys apparently possess both excellent fabricability and high-temperature strength, and one class of alloys would suffice for target purposes.

The target properties for the seven classes of alloys considered in the Refractory Metal Sheet Rolling Programme are shown in Tables I, II, and III. The room-temperature targets were intended to determine whether or not the alloy would have a ductile-to-brittle transition below room temperature. Indeed, it is expected that the tantalum alloy will remain ductile down to below -320°F. Notch sensitivity and bend transition temperature are other parameters where the more fabricable and ductile materials are given more demanding target properties to reflect their greater capabilities in these respects. Weldability is expected to be excellent in fabricable columbium and in tantalum alloys, marginal in fabricable molybdenum, and high-strength columbium alloys, and is not required in high-strength molybdenum or tungsten alloys. A number of properties not amenable to numerical target properties should also be considered in the selection of alloys. These include: density, melting point, emissivity, modulus of elasticity, thermal shock resistance, creep properties, oxidation resistance and contamination, coatability, experience with 45° brittleness, and lamination tendency.

A number of problems must be solved before utilization of the refractory metals. The coating problem is especially urgent. A number of recent laboratory developments encourage the hope that the coating problem will be solved for the leading edge application, at least. Fortunately, the times involved during oxidation exposure are much shorter than are usually considered in elevated-temperature applications. Typical examples include 1/2-hour exposures up to 2,500 to 3,000°F for about 5-10 excursions. The coatings will be applied to structures after assembly, in many cases, and ability to withstand creep strain is not a major requirement. Hence, requirements for ductility are less severe than in the former potential refractory metal application in the turbine stage of turbojet engines. A cementation-type coating, designated W-2, looks promising for molybdenum. In columbium alloys, aluminium-silicon dipped or sprayed coatings and aluminium-oxide-base coatings have shown encouraging results. Also, hot dipped or sprayed zinc coating has shown exceptional promise for short-time exposures up to 2,000°F and in addition possess excellent self-healing tendencies. Zinc may be especially promising as an in-process coating to avoid contamination during fabrication.

The development of refractory metal sheet is off to a good start. Formidable problems are involved in production and utilization of these materials in advanced airframe and propulsion structures. If these vehicles are to be built, the problems will have to be solved. Suffice it to say that the next several years should be extremely interesting.

ELECTRON BEAM FUSION AND ITS APPLICATIONS

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SUMMARY

A general account is given of the principles involved in the production and utilisation of electron beams for fusion applications. A more detailed discussion is made of the advantages of the process over induction or arc fusion methods for welding, ingot production and zone refining from a metallurgical and operational point of view. Details are given of equipment under development for ingot production and zone refining.

INTRODUCTION

In recent years increasing interest has developed in the application of electron bombardment heating as a convenient means of achieving fusion in high vacuum.

The main impetus has resulted from the conclusive proof that the properties of materials are markedly influenced by impurities. This is particularly so in the case of the refractory metals. In molybdenum, for example, as shown by workers at the Battelle Memorial Institute, U.S.A.¹, oxygen concentrations of the order of only a few parts per million have a pronounced effect on the ductile-to-brittle transformation temperature. In other fields too, notably semi-conductors, the influence of trace impurities has been shown to be of the utmost importance. It is probably true to say that it was in this field that this fact was first appreciated, and in which the use of electron beam fusion methods were first utilised.

The potential of electron beam fusion methods arises not only from the presence of high vacuum, but from the fact that controlled, localised fusion can be conveniently achieved. By efficient beam focussing very much higher heat inputs per unit area are possible than by other means of heating. This is particularly important in zone refining and welding applications, as will be discussed later. The advantage of the process in minimising atmosphere contamination is illustrated by the fact that a vacuum of 10^{-4} mm Hg contains only 0.1 part per million of the atmosphere originally in the system, while argon of 99.99% purity contains 100 parts per million of impurities.

General electrical considerations

The basic electrical system necessary for the production of a focussed electron beam is comparatively simple and will apply to each of the applications to be discussed.

Fig. 1 shows diagrammatically the general arrangement. A high negative potential is applied to an electron emitter. This is often a tungsten filament heated by a low voltage supply, or, for high power guns, is sometimes an indirectly heated surface

coated with a layer of material of high electron emissivity. This is a more convenient way of achieving a large emitting surface than by using a tungsten wire. The electrons are accelerated from the filament towards and pass through a hollow anode, usually at earth potential. A modulator grid is often placed between the filament and anode which collimates the beam and which is also often used as an alternative or additional

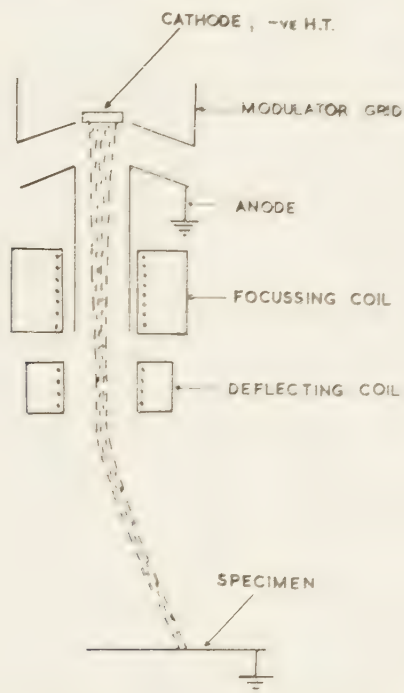


Fig. 1. Schematic diagram of electron beam production, focussing and deflection.

means of focussing. By applying a bias potential more negative than the filament the electrons are electrostatically repelled to a narrower beam, thus achieving focussing. The dimensions, shape and position of the filament, modulator grid and anode relative to one another are very critical. For example in X ray tubes, the filament may have to be positioned to within 0.002 in. relative to the grid to obtain accurate focus. Most modern guns are designed to follow the 'Pierce space charge principle'. In this, the anode and modulator are shaped and positioned so that the equipotential lines between the two follow a definite pattern relative to the electrons emerging from the cathode. A much improved degree of focussing is possible if the Pierce system is followed.

The focus of the electron cloud emerging from the anode is further controlled by magnetic solenoid or electrostatic field focussing. With advanced types of electron guns the focussed spot can be as small as 0.01 mm², achieving very high heat inputs per unit area, but even with very simple optics, neglecting all of Pierce's principles, a spot size of 1-2 mm is easily obtainable.

Further, electromagnetic deflection of the beam focus forms a convenient way of positioning the focussed spot on the specimen being melted. Indeed, one welding equipment under development uses electromagnetic deflection as a means of continuous traverse of the weld pool over the specimen.

In certain welding applications a pulsed beam is required. A convenient way of achieving this is to pulse the voltage on the modulator grid. A critical "black-out voltage" exists for a given beam power at which the electrons are prevented from emerging through the grid by the negative field. This is conveniently achieved by a simple electronic timing circuit coupled to the bias circuit, which gives a superimposed pulsed voltage to the modulator grid additional to any bias used for focussing to bring the total up to the black-out voltage.

A further advantage of electron beam fusion is that in addition to round spots, shaped heat inputs can be produced. In principle, the shape of the cathode can be accurately reproduced. Thus line foci can be attained which enable long, narrow heat inputs to be produced. This is of advantage in zone refining and melting applications, as will be described later.

The heating effect at the specimen is related to the kinetic energy of the electron beam. This is determined by

- (a) the speed of the electrons determined by the accelerating voltage,
- (b) the number of electrons in the beam hitting the specimen. This factor — the beam current — can be increased by greater filament heating current or surface area.

However, there are certain limitations to the power increase possible for a given application. Increasing the H.T. increases the intensity of X-ray emission and so increased shielding of this hazard may be necessary. About 40 kV is considered the safe limit for a $\frac{1}{4}$ in. thick chamber. Viewing becomes a further problem owing to this hazard, and thick lead glass windows or indirect viewing by mirrors may be necessary. Increasing the beam current to produce more electrons gives complications owing to the space charge effect (mutual repulsion of the electrons in the beam). This limits the minimum size of focussed spot and thus has to be considered where fine focus heat inputs are required.

Welding applications

The first application of electron beam fusion for joining was undertaken by the French Atomic Energy Establishment at Saclay, by J. A. STONER². Since then considerable interest has developed and commercial units are available in this country, U.S.A. and Germany.

In addition to the obvious advantage of high vacuum operation, the high degree of control of the welding variables, notably heat input, possible by electron beam welding makes the process particularly attractive. Variation of filament current, voltage or focus allows simple finger tip control of heat input conditions during the welding operation. The excellent quality of welds produced by this method are a good illustration of the control achieved. Fig. 2 shows the appearance of a typical molybdenum weld of an end cap in a tube. Low heat inputs over a large area of the work by use of a diffuse focus allow pre and post heating of the weld area to an extent that is not possible in arc welding owing to arc instability. This is particularly useful in materials which are susceptible to hot cracking or which would normally require some heat treatment after welding. A further significant advantage is the fact that

very much higher heat inputs per unit area are possible than by arc welding. The consequence of this is that greater penetration is possible for a given pool area, Fig. 2. Penetration to width ratios up to 3 : 1 have been achieved³. The criterion here is to use high kV and low beam currents to obtain a small focus with maximum power. The trend in the German and American equipment is now to use high voltage guns, and equipments of up to 150 kV are under development.

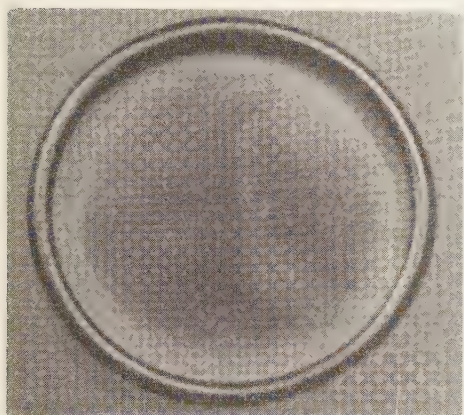
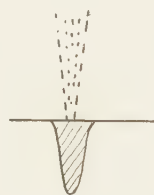


Fig. 2. Molybdenum tube-end cap electron beam welded.



ARGON ARC



ELECTRON BEAM

Fig. 3. Comparison of molten pool in fusion welding.

The attainment of fine focus heat inputs facilitates the welding of very thin material, conversely in the welding of thick materials, high penetration to width ratios result in a much smaller volume of coarse grained weld material for a given penetration. This results in a further advantage in that the extent of the heat affected zone is reduced. These two factors result in improved mechanical properties. For example, the impact strength of zirconium alloys³ is doubled in electron beam welded material compared with argon tungsten arc welds as a result of these factors. A comparison with unwelded parent material showed the improvement due to lack of atmosphere contamination was of less importance than the reduced weld area and heat affected zone in this example. However, in the case of the refractory metals, particularly molybdenum and tungsten where impurity content is a much more important factor in mechanical properties the lack of impurity pick up from the welding atmosphere is of much greater importance. The attainment of vacuum melting in the welding process affects a purification of the weld bead by the release of volatile impurities, *e.g.* oxide in molybdenum, and greatly increased bend ductilities have been obtained in molybdenum welded by this method compared with inert gas arc welding. However, one must not neglect the embrittlement effect caused by the redistribution of impurities on recrystallisation inherent in the behaviour of the parent metal. The vacuum melting purification of the weld pool will have little effect on the properties of the metal in the recrystallised heat affected zone. While the attainment of narrow deep weld pools minimises the extent of the heat affected zone, a complication arises in the case of materials which are likely to evolve gas on vacuum melting, since

porosity may be encountered. Multiple pass welding at low speeds may have to be used to de-gas satisfactorily the weld zone. This problem has been encountered in molybdenum and niobium welds made by the electron beam process.

The principle problem in electron beam welding is the release of vapour into the chamber, whether it be from included volatiles or the inherent vapour pressure of the material. Apart from coating the chamber and gun with vapourised metal, if the rise in pressure becomes excessive electrical breakdown by discharge can occur. While for normal materials this problem is not significant, in the case of highly volatile materials a pulsing technique is utilised in which welding is carried out in short bursts. During the time the beam is off, the high pumping capacity of the equipment removes the released vapour before the beam comes on again and re-melting occurs, thus minimising pressure build up.

From an economic point of view it has been suggested⁴ that the electron beam welding process has significant advantages over the vacuum purged inert gas chamber arc welding method normally used for the refractory metals. Neglecting capital cost of equipment and comparing only consumable costs (electrical power and inert gas used, etc.) the ratio is of the order of 35:1 cheaper for the electron beam process.

Melting applications

Before the development of electron beam melting techniques the two most common processes for vacuum melting and casting were by H.F. induction or consumable arc furnaces. For high purity materials H.F. induction must be excluded since the crucible and mould materials necessary will contribute to impurity pick-up. The development of consumable arc furnaces went a long way towards achieving a process by which large ingots could be produced in vacuum. Impurity pick-up from crucibles was eliminated and mould contamination minimised by the use of water-cooled copper moulds. Very large furnaces producing ingots up to 24 in. diameter are in commercial use.

While retractable moulds have been used, the normal method is to melt the ingot into a fixed mould, starting at the bottom and feeding in the electrode. However, by this process the melting conditions attained in the consumable arc furnace, while minimising impurity pick-up, are not optimum for vacuum purification of the metal by release of volatile impurities. Melting is continuous since the heat input depends on the maintenance of the arc, which necessarily means continuous feed of the electrode. Prolonged exposure of the molten surface which would facilitate release of volatiles is thus not possible. Satisfactory arc conditions require fairly short arc lengths and thus, particularly in the case of the fixed mould, release of volatiles is restricted by the confined geometry of the system.

The addition of alloying material or reclamation of scrap by hopper feeding is very difficult owing to possible shorting of the arc. All material to be melted has therefore to be fabricated to electrodes.

Electron beam melting techniques overcome to a large extent the limitations of consumable electrode arc furnaces.

(1) By suitable electron optics the molten pool conditions can be controlled to a greater degree. The width, depth and temperature of the pool can be controlled by variation of the power input and focussed area. This can be attained irrespective of rate of addition of material to be melted.

(2) The improved control over melting rate ensures optimum conditions for release of volatile impurities, less likelihood of re-entrapment of dross, minimum trouble from porosity and improved control of solidification compared with the arc melting method.

(3) In addition to the melting of solid consumable electrodes, the production of vacuum melted ingots is possible from swarf or small scrap material without the need for electrode fabrication. Alloy additions can also be conveniently made by this method. The vacuum reclamation of scrap material directly into ingots is of particular potential.

The main difficulty with electron beam melting furnaces is the problem of pressure rise due to volatilisation of impurities and of the metal itself. This can cause electrical discharge breakdown in the electron gun. The normal way of overcoming this is to isolate the gun in an evacuated chamber, separated from the main evacuated furnace chamber by a diaphragm with an aperture large enough to allow passage of the electron beam stream, but small enough to attain the required pressure differential.

Loss of metal due to evaporation can become a serious problem in the case of metals with a high vapour pressure. Loss of ingot weight, which may be up to 20%, is unavoidable. However, this can be reclaimed by the incorporation of condensor plates of the metal concerned suitably positioned relative to the melt. The evaporated metal deposits on these and the plates can be subsequently remelted.

In the case of highly volatile metals, viewing has to be carried out indirectly by

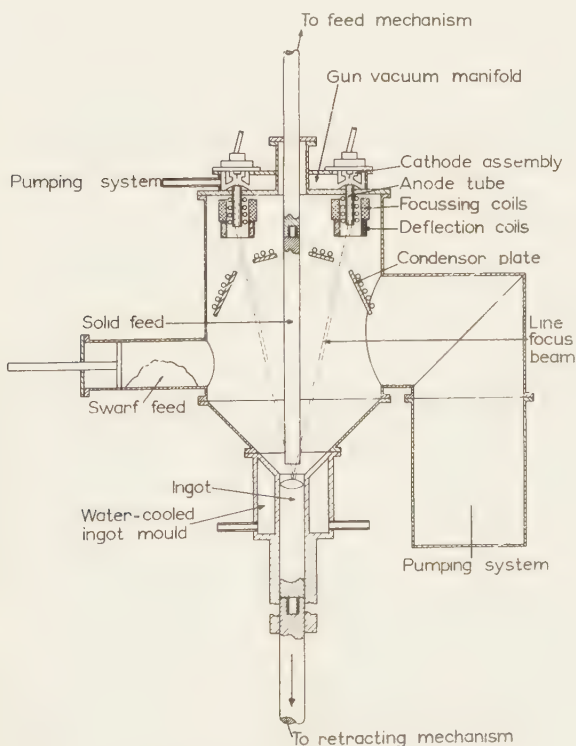


Fig. 4. Multiple gun electron beam melting furnace.

mirrors, the optical qualities of which are not impaired by depositing metal. The mirror system of viewing is also of advantage in shielding from the X-ray hazard. The approach of American investigators into electron beam furnaces has been reported in a conference held at the Alloyd Research Corporation, U.S.A., in March 1959⁵, and hence it is not proposed to discuss their work in detail in this paper. Furnaces of 100 kW capacity melting up to 6 in. diameter ingots are under development, and results have shown that the impurity content of molybdenum ingots, for example, can be reduced below the limit detectable by their normal analytical methods.

Within the A.E.I. group, work has commenced on the development of an electron beam melting furnace of up to 100 kW total power distributed in a multiple gun system, to produce $2\frac{1}{2}$ in. diameter ingots from the refractory metals, zirconium and beryllium. A retractable mould technique is to be used utilising solid rod with the alternative of hopper feed for swarf and scrap melting. A diagram of the proposed unit is shown in Fig. 4.

Multiple electron guns of the Pierce system design will be used. A three-gun system can operate on an unrectified three-phase supply, connecting one to each phase and utilising the self-rectification property of the electron gun. However, four guns are considered optimum, and these operating from one power pack would require a more expensive rectified power unit. The guns are positioned symmetrically within a separately evacuated manifold "O" ring sealed to the top of the melting chamber which is connected to its own large vacuum pumping system. The vacuum in the two chambers is separated by a fairly long water-cooled tube in line with each gun. A tube effects a greater impedance to the pressure differential than a plate aperture normally used for this purpose. Thus a high vapour pressure can be tolerated in the melting chamber without impairing the vacuum in the gun manifold. Magnetic focussing coils are positioned around each of the tubes to focus the electron beam. At the end of the tubes, magnetic deflection coils are placed to deflect and control the position of the focussed beams on the ingot mould. An additional advantage of the deflected beam and long tube is that with this arrangement, positive ion bombardment of the cathode is eliminated resulting in increased cathode life. Each of the guns utilises a line focus electron source. This results in intersecting beams, giving a large heating area. The focus and direction of the beams can be adjusted to provide a convenient means of control of the size of the molten pool. When using solid rod feed, it could be arranged, for example, to have some of these beams positioned to impinge on the rod to allow drip feed of the rod into the molten pool. Additional purification by volatilisation of impurities could occur from these drops. A retracting mould assembly will be used for continuous production of ingots, metal feed being by a vertical solid rod mechanism with additional hopper feed for alloying, additions or scrap melting. The H.T. variable up to 100 kV will be distributed between the guns, the individual power of each being adjusted by control of cathode emission. Adequate X-ray shielding is necessary, a mirror system being utilised for viewing, together with provision of condenser plates.

Zone refining

Zone refining was perhaps one of the first applications of electron beam fusion⁶, and it has been shown that high purity refractory metals, of greatly improved mechanical properties, can be produced by this means⁵. The method is superior to

induction methods since more efficient heat input is obtained and narrower zones are achieved.

The methods that have been used are principally based on the Calverley apparatus in which a ring tungsten filament surrounds a vertical rod specimen. A high potential is applied between the heated tungsten cathode and the rod, the electrons impinging on the specimen melting a localised zone. In recent equipments, improvements have been made in focussing by the incorporation of electrostatic deflection plates. However, there are certain limitations to these electron beam zone refining designs.

(1) Pressure build up due to volatilisation can cause arcing and electrical breakdown, thus limiting the H.T. voltage that can be used. Increased power is therefore only attained by increased beam current and so focussing is impaired.

(2) As a result of (1) the heat input possible is limited since wide zones are produced. PFANN⁷ has shown that for efficient zone refining a narrow zone is necessary. Further, wide zones lead to difficulties owing to possible collapse of the molten zone.

(3) Contamination of the filament by condensate from the specimen can occur.

(4) Positive ion bombardment of the cathode is likely to be severe, thus limiting cathode life.

An equipment under development in the A.E.I. group for zone refining is shown in Fig. 5. This is basically an additional application of the gun design used in the ingot melting furnace. In this, three line focus guns are arranged symmetrically around a

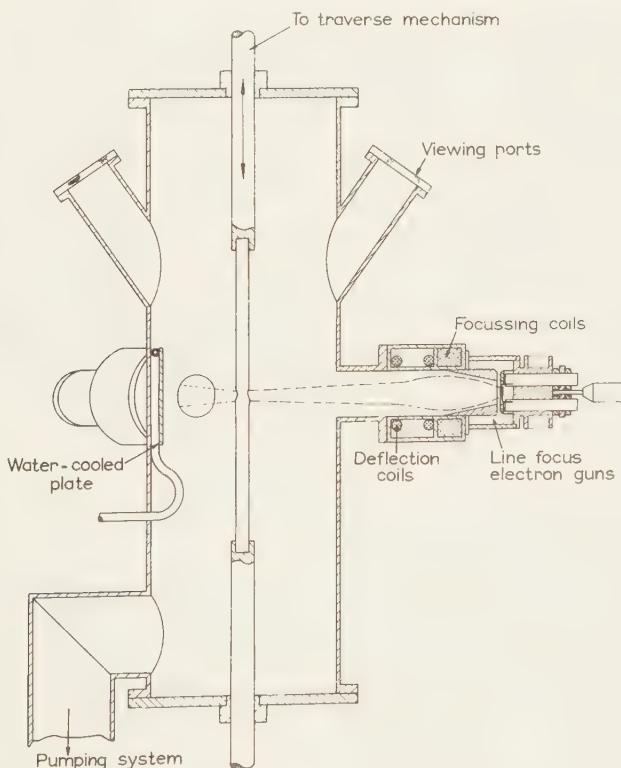


Fig. 5. Multiple electron gun zone refining.

chamber so that the focussed beams impinge horizontally on a vertical ingot specimen. Water-cooled plates are positioned opposite the guns to kill any beam passing the specimen. The deflecting coils assist in the positioning of the focussed beams to achieve a symmetrical zone. The advantages of this system are

(1) The use of high kV with moderate currents allow fine focus of the beam and so result in very high heat input per unit area. As shown in the electron beam welding studies, this results in high penetration to width ratios in the molten pool. Thus larger diameter specimens can be zoned by this method than is possible with the normal zone refining equipments.

(2) The greatly increased distance of gun to specimen,

(a) allows greater release of volatiles by evaporation,

(b) by the use of the separately evacuated gun enclosure obviates discharge breakdown,

(c) eliminates filament contamination by condensed vapour.

(3) The use of magnetic lenses for focussing and deflection enables improved control and positioning of the heat input.

(4) The use of the deflected beam and tube eliminates positive ion damage to the cathode.

(5) A non-mechanical traverse system is also possible by continuous magnetic deflection of the beams.

CONCLUSIONS

The advantages of electron beam fusion over arc or induction methods for welding, ingot production and zone refining can be summarised as

(1) Increased control of the operational variables.

(2) Optimum purification by improved vacuum and other operational conditions.

(3) More efficient utilisation of available power, particularly in relation to heat input per unit area.

The equipments under development within A.E.I. obviate to some extent the limitations associated with other electron beam melting and zone refining designs.

Using the equipments described, prior electron beam vacuum melting of refractory metal stock to ingots to remove volatile impurities, followed by electron beam zone refining of this ingot to remove non-volatile impurities, prior to subsequent fabrication, illustrate the envisaged application to the purity problem in the refractory metals.

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II. Constitution, Structure and Physical Properties

NIOBIUM AND TANTALUM ALLOYS

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SUMMARY

Recently published work on niobium and tantalum alloys is briefly reviewed. This is followed by a consideration of the strain energies associated with solid solution formation in some binary systems, which shows that the strain energy contribution may account for differences in alloying behaviour between certain niobium and tantalum alloys. Finally, original work on several niobium and tantalum systems is described.

INTRODUCTION

The constitution of alloys of niobium and tantalum has not been extensively studied, and very few complete phase diagrams are available. The recent book by MILLER¹ contains a detailed and comprehensive review of all but the latest work on the constitution of the alloys, and in view of this, the present paper will limit the consideration of previous work to a brief survey of data recently published or not included in MILLER's book.

Niobium and tantalum are both body-centred-cubic transition elements from the same Group, Va, of the Periodic Table. Also, their atomic diameters are virtually identical (2.95 Å) and the melting points of the metals are high (niobium 2,468°, tantalum 3,000°C). Consequently, very marked similarities in the alloying behaviour of niobium and tantalum with other elements are to be expected. In the present paper, certain differences in the behaviour of niobium and tantalum are considered, based on the strain energy accompanying solid solution formation.

In addition, previously unreported work from this Laboratory on the constitution of binary niobium and tantalum systems is described.

RECENTLY PUBLISHED WORK ON NIOBIUM AND TANTALUM ALLOYS

Aluminium-niobium

McKINGSEY AND FAULRING² identified a new intermetallic phase in the aluminium-niobium system at the composition Nb₂Al. The structure of this phase is the σ type, with $a_0 = 9.943$, $c_0 = 5.186$ Å, $c/a = 0.522$.

Nb₂Al is of particular interest, being the first reported sigma phase which does not contain a pair of transition metals from the Long Periods.

Beryllium-niobium

At least three intermediate crystal types occur in the beryllium-niobium system.

NbBe_{12} has a tetragonal structure (ThMn_{12} type). Several workers have reported^{3,4,5} lattice spacings for this compound.

ZALKIN, SANDS AND KRIKORIAN determined the crystal structures of $\text{Nb}_2\text{Be}_{17}$ ⁶ and Nb_3Be_2 ⁷. The former is rhombohedral with $a = 5.599 \text{ \AA}$, $\alpha = 82.84^\circ$. Nb_3Be_2 has a tetragonal structure with $a = 6.49$, $c = 3.35 \text{ \AA}$, $c/a = 0.517$.

Beryllium-tantalum

As in the beryllium-niobium system, a compound of the ThMn_{12} type exists at TaBe_{12} . Lattice spacings are given in several publications^{4,5,8}.

Cerium-niobium

Niobium rich alloys were investigated by SAVITSKII, TEREKHOVA AND BUROV⁹. Extensive regions of solid and liquid immiscibility exist in the system, with the monotectic horizontal at $2,370 \pm 20^\circ\text{C}$. Niobium lowers the transition temperature of cerium by $20\text{--}25^\circ\text{C}$, but solid solubilities were shown to be very small.

Chromium-tantalum

The phase diagram has been studied by GRIGOR'EV, KUPRINA AND NEDUMOV¹⁰ by thermal and metallographic methods. One compound is present in the system, Cr_2Ta , melting congruently at $2,020^\circ\text{C}$. The compound exists in two modifications with a transition temperature of $1,805^\circ\text{C}$. Two eutectics occur in the system: $\text{Cr}/\text{Cr}_2\text{Ta}$ at $1,700^\circ\text{C}$, 13 at. % Ta, and $\text{Cr}_2\text{Ta}/\text{Ta}$ at $1,980^\circ\text{C}$, 46 at. % Ta. The solubility of tantalum in chromium at the eutectic temperature is 1.5 at. %, and chromium in tantalum 28 at. % at $1,800^\circ\text{C}$.

Iridium-niobium

DWIGHT AND BECK¹¹ identified a new Cu_3Au type structure of composition NbIr_3 with $a_0 = 3.893 \text{ \AA}$.

Iridium-tantalum

Although no superlattice lines were observed, DWIGHT AND BECK¹¹ suggest by analogy with NbIr_3 that a Cu_3Au ordered phase TaIr_3 exists with $a_0 = 3.889 \text{ \AA}$.

Molybdenum-niobium

KORNILOV AND POLIAKOVA¹² confirm complete solid solubility in the molybdenum-niobium system and show that a minimum occurs in the liquidus near 80% niobium.

Niobium-rhenium

Some ordering of the χ phase (α -manganese type) in the niobium-rhenium system was detected by NIEMIEC AND TRZEBIATOWSKI¹³.

The full system was studied by SAVITSKII, TYLKINA AND POVAROVA¹⁴. A large solid solution region of rhenium in niobium, extending to 46.5 at. % rhenium, is present in the system. Only one intermediate phase, χ , is shown forming peritectically at $2,520^\circ\text{C}$ from rhenium and the melt. Niobium and χ form a eutectic at $2,350^\circ\text{C}$, at. 50% rhenium. The solubility of niobium in solid rhenium was not determined precisely.

Niobium-rhodium

It is reported by DWIGHT AND BECK¹¹ that NbRh₃ is of the Cu₃Au ordered type, although superlattice lines were not observed. The lattice spacing is given as $a = 3.865 \text{ \AA}$.

Tantalum-rhodium

An analogous phase TaRh₃ with $a = 3.86 \text{ \AA}$ occurs as an ordered Cu₃Au type in the tantalum-rhodium system¹¹.

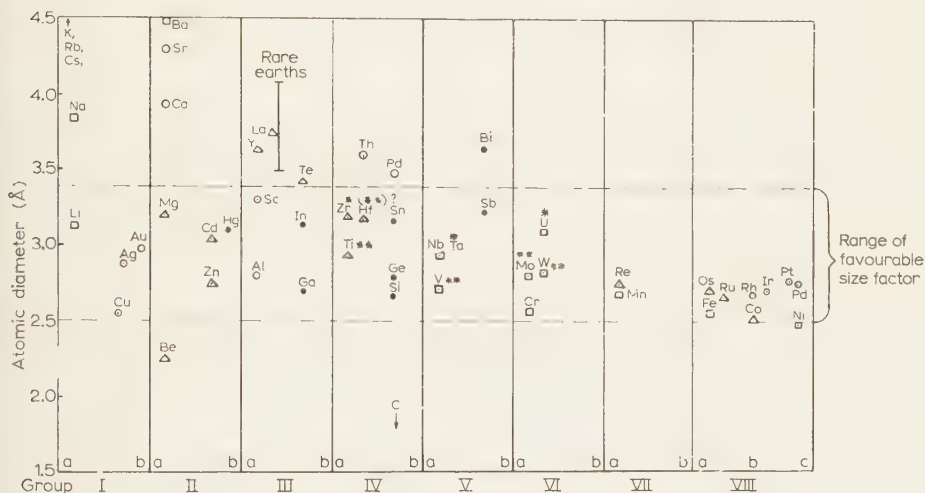


Fig. 1. Favourable size factors for solid solution formation in niobium and tantalum. $\square$, BCC; $\circ$, FCC; $\triangle$, HCP; $\bullet$, others; $*$, CSS with Nb; $**$, CSS with Nb and Ta.

SOLID SOLUTION FORMATION IN NIOBIUM AND TANTALUM ALLOYS

Niobium and tantalum have favourable size factors towards neighbouring elements in the Periodic System (Fig. 1) and hence form wide or complete ranges of solid solutions with these elements. On simple size factor considerations, no discrepancies would be anticipated between alloys of niobium or tantalum, and other factors must be responsible for the differences in alloying behaviour observed. It is known that the binding energy of niobium is significantly less than that of tantalum (*e.g.* the heats of sublimation are 169 and 183 kcal/mole respectively). On this basis, HOWLETT¹⁵ has considered the strain energy contribution to solid solution formation in uranium alloys and found that it satisfactorily accounts for the low solid solubility of tantalum compared with niobium, in γ -uranium. Also, the strain energy contribution was found to pass through a maximum at the composition corresponding to the maximum of the miscibility gap in certain uranium systems. HOWLETT's treatment has now been applied to miscibility gap formation in the binary systems of zirconium with niobium or tantalum.

For estimating the strain energy contribution HOWLETT used the expression originally proposed by LAWSON¹⁶, *viz.*

Strain energy =

$$\frac{2}{3} \cdot \frac{G_A}{V_A} (V_B - V_A)^2 c^2 (1 - c) + \frac{2}{3} \cdot \frac{G_B}{V_B} (V_B - V_A)^2 c (1 - c)^2 \quad (1)$$

where G_A is the rigidity modulus of pure A , G_B the rigidity modulus of pure B , V_A the molal volume of pure A , V_B the molal volume of pure B , and c the atomic fraction of A atoms.

By differentiating this expression, the alloy composition corresponding to maximum strain energy is given by

$$3 \left(\frac{G_B}{V_B} - \frac{G_A}{V_A} \right) c^2 + 2 \left(\frac{2 G_B}{V_B} - \frac{G_A}{V_A} \right) c + \frac{G_B}{V_B} = 0 \quad (2)$$

It was postulated by HOWLETT that the temperature at which a miscibility gap forms in the solid state is some function of the strain energy of the solid solution. Thus, the greater the strain energy the higher the temperature at which the gap will form. In addition, the composition of maximum strain energy, calculated from eqn. 2, should correspond with the observed composition of the miscibility gap maximum.

In these calculations, it is necessary to use values of the rigidity moduli and molal volumes at the temperatures under consideration. However, little data are available on rigidity moduli at elevated temperatures, and in certain cases HOWLETT estimated the required rigidity modulus from the high temperature Young's modulus, assuming that Poisson's ratio (values available at room temperature) remains constant with change of temperature. Miscibility gaps form in the niobium-uranium and niobium-zirconium systems near 950°C, and this temperature has been used as a basis for the calculations. Values of the rigidity moduli and lattice spacings given by HOWLETT are listed in Table I.

TABLE I
RIGIDITY MODULI AND LATTICE SPACINGS AT 950°C

<i>Metal</i>	<i>Rigidity modulus (kg mm²)</i>	<i>Lattice parameter (Å)</i>	<i>Molal volume V (cm³)</i>
Niobium	1900	3.315	10.97
Tantalum	6154	3.326	11.08
Titanium	1397	3.315	10.97
Zirconium	1200	3.615	14.23
Uranium	2000	3.533	13.28

The calculated maximum strain energies for a series of niobium and tantalum binary systems are given in Table II. The values form a consistent pattern with the experimental observations (Fig. 2) on the systems considered, and the calculated and observed compositions of the miscibility gap maxima are in good agreement. Thus, the binary systems of niobium or tantalum with titanium have very low strain energies (0 and 2 cal/mole respectively) associated with their solid solutions, and continuous solid solubility occurs in these systems above the β - α titanium transition temperature. The higher maximum strain energies of niobium-uranium and niobium-

TABLE II

STRAIN ENERGY VALUES FOR SOLID SOLUTION FORMATION

System	Calculated composition of maximum strain energy	Calculated maximum strain energy (cal/mole)	Remarks
Nb-Ti	—	0	Continuous solid solubility
Ta-Ti	37 at. % Ti	2	Continuous solid solubility
Nb-U	49 at. % U	310	Miscibility gap at 50 at. % U
Nb-Zr	43 at. % Zr	500	Miscibility gap at 40 at. % Zr
Ta-U	38 at. % U	675	Limited mutual solubilities
Ta-Zr	44 at. % Zr	1300	Limited mutual solubilities

zirconium solid solutions result in the formation of a miscibility gap near 950°C in niobium-uranium alloys, and at ~ 1,000°C in niobium-zirconium alloys, *i.e.* although continuous solubility occurs between the body-centred-cubic forms of the elements at high temperatures, breakdown into two body-centred-cubic phases takes place at lower temperatures.

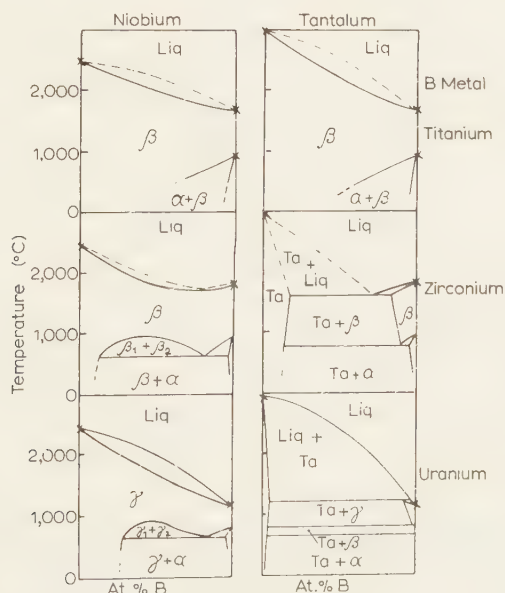


Fig. 2. Solid solution behaviour in certain niobium and tantalum systems.

In the other tantalum systems considered in Table II, (Ta-U, Ta-Zr), the miscibility gap at 950°C is much wider, and limited mutual solid solubilities in the body-centred-cubic phases are present up to the solidus temperature. The low solubilities are attributed to the high strain energies which would be associated with the formation of extensive body-centred-cubic solid solutions in these systems.

It is concluded that the strain energy approach proposed by HOWLETT is consistent in explaining alloying behaviour differences between niobium and tantalum with certain neighbouring elements in the Periodic System, *i.e.* when marked electronic interaction and compound formation are absent.

NIOBIUM AND TANTALUM ALLOY STUDIES

Complete investigations have been made in this Laboratory of two niobium systems, niobium-rhenium and niobium-zirconium. In addition a number of more limited studies have been made on several other niobium and tantalum systems, mainly as a follow up to the earlier reported survey of certain transition metal systems for sigma phases¹⁷. The results obtained from these investigations have not been previously reported and are given below.

Niobium-rhenium system

The phase diagram of the niobium-rhenium system is given in Fig. 3. Two intermediate phases occur, one with the sigma structure (σ) and the other of the α -man-

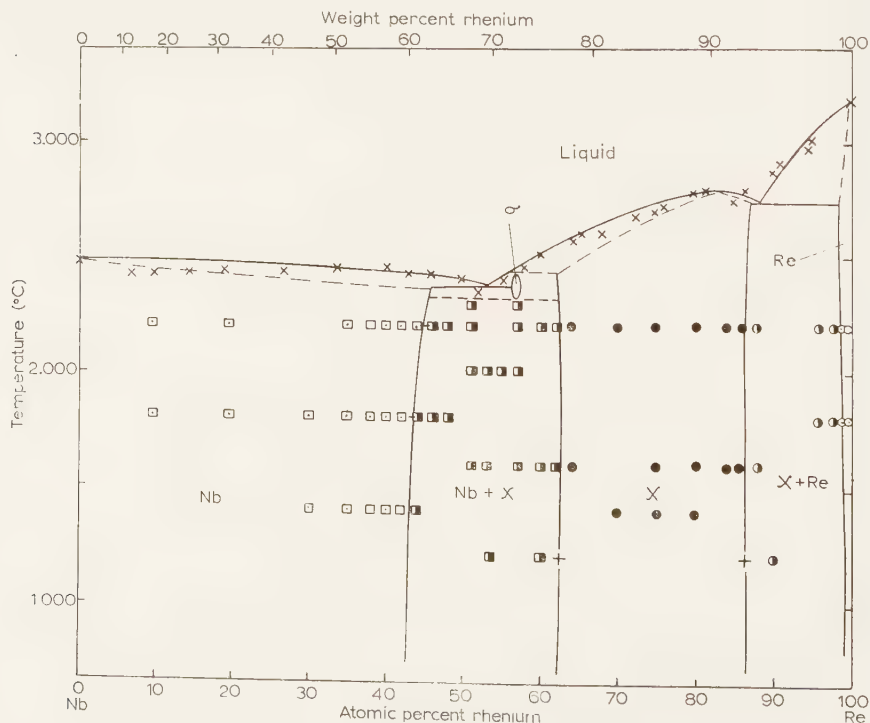


Fig. 3. The niobium-rhenium system. $\square$, Nb; $\blacksquare$, Nb + χ ; $\bullet$, χ ; $\circ$, χ + Re; $\odot$, Re; $\times$, melting points; +, X-ray solubilities.

ganese type (χ). The niobium solid solution extends to 46 at. % rhenium at 2,400°C, the eutectic temperature between niobium and sigma. The solid solubility falls little with temperature to about 43 at. % rhenium at 1,000°C.

The sigma phase could be detected in arc-melted alloys only. Annealing samples at temperatures up to 2,300°C, followed by water quenching, resulted in decomposition of sigma into χ and niobium solid solution. Consequently, it is considered that sigma exists over only a small range of compositions and temperatures. Metallographic studies confirm that the sigma phase forms peritectically from χ and the melt near 57 at. % rhenium.

The χ phase has a large homogeneity range, 62–87 at. % rhenium, and melts congruently at 2,800°C. A small minimum in liquidus values near 88 at. % rhenium was shown from metallographic examination of arc-cast alloys to correspond with a χ /rhenium eutectic at 2,730°C. The solid solubility of niobium in rhenium is low, and has been placed at about 1½ at. % at the eutectic temperature.

A fuller account of the niobium rhenium investigation is to be published¹⁸, which includes lattice spacings of χ and the niobium base solid solution, and metallographic corroboration of the other features of the diagram. It should be noted that the solid solubility of rhenium in niobium and the extensive χ field are in good agreement with the recently published diagram by SAVITSKII, TYLKINA AND POVAROVA¹⁴, but these workers do not appear to have studied the mode of formation of sigma, χ or the rhenium base solid solution.

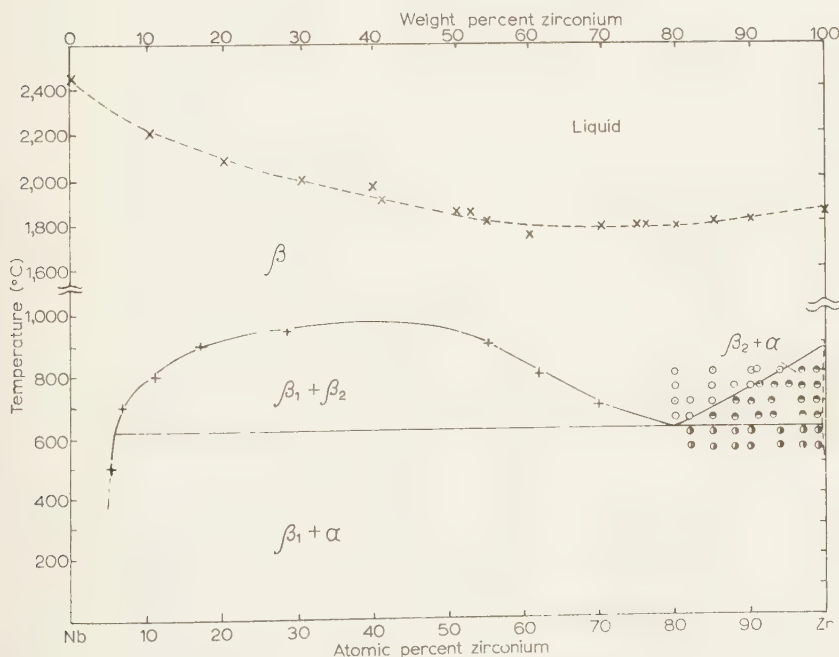


Fig. 4. The niobium-zirconium system. $\times$, melting points; $\odot$, β ; $\bullet$, $\beta_2 + \alpha$; $\ominus$, $\beta_1 + \alpha$; +, X-ray solubilities.

Niobium-zirconium system

Results from the investigation of the niobium-zirconium system are incorporated in the diagram given in Fig. 4. Liquidus values were determined by an arc furnace optical pyrometer technique¹⁹, and showed a flat minimum near 60 at. % zirconium, 1,750°C.

Continuous solid solubility at elevated temperatures between niobium and β -zirconium was confirmed by X-ray methods. Lattice spacings were determined from thin cylindrical specimens, etched to suitable dimensions from rolled 0.048 in. square section rods. The rods were homogenised at temperatures just below the solidus in evacuated sealed-off glass vessels by direct passage of electric current. The cooling rate of the rods after switching off the current was sufficiently high to retain the body-centred-cubic solid solution without decomposition. The lattice spacing results obtained are given in Fig. 5 and Table III.

At lower temperatures, the β solid solution dissociates into a two body-centred-cubic phase field ($\beta_1 + \beta_2$), *i.e.* a miscibility gap occurs in alloys of intermediate composition. The limits of this two phase field were determined by X-ray methods

TABLE III
LATTICE SPACINGS OF NIOBIUM-ZIRCONIUM ALLOYS

Composition (at. % Zr)	Annealing temperature (°C)	Lattice spacing (Å)	
0	1,500	β 3.307 ₄	
5	1,800	β 3.318 ₂	
10	1,800	β 3.330 ₄	
20	1,600	β 3.359 ₈	
20	700	β_1 3.317 ₇	
20	500	β_1 3.314 ₉	
30	1,800	β 3.391 ₅	
30	950	β_1 3.382	
30	700	β_1 3.323 ₄	
30	500	β_1 3.315 ₄	
40	1,500	β 3.419	
40	900	β_1 3.348 ₇	
40	800	β_1 3.336 ₈	
40	700	β_1 3.323 ₅	
40	500	β_1 3.317 ₀	
50	1,600	β 3.447 ₂	
50	900	β_1 3.352 ₂	β_2 3.461 ₈
50	800	β_1 3.335 ₅	β_2 3.478 ₂
50	700	β_1 3.322 ₇	
50	500	β_1 3.316 ₇	
60	1,600	β 3.483 ₆	
60	800	β_1 3.335 ₀	β_2 3.482 ₀
60	700	β_1 3.325 ₁	β_2 3.505 ₆
70	1,600	β 3.503 ₇	
70	700		β_2 3.503 ₅
80	1,600	β 3.533 ₈	

(Fig. 5 and Table III). Small homogenised rod samples, or filings from homogenised alloys, were annealed and quenched for lattice parameter measurements in the $\beta_1 + \beta_2$ field.

The zirconium-rich region of the diagram was established chiefly by metallographic examination of quenched alloys. The β - α transition in zirconium is depressed on addition of niobium to a monotectoid, which has been placed at 610°C, 80 at. % zirconium. The solid solubility of niobium in α -zirconium is low, < 1 at. % at the monotectoid temperature. The monotectoid horizontal extends to 94 at. % niobium.

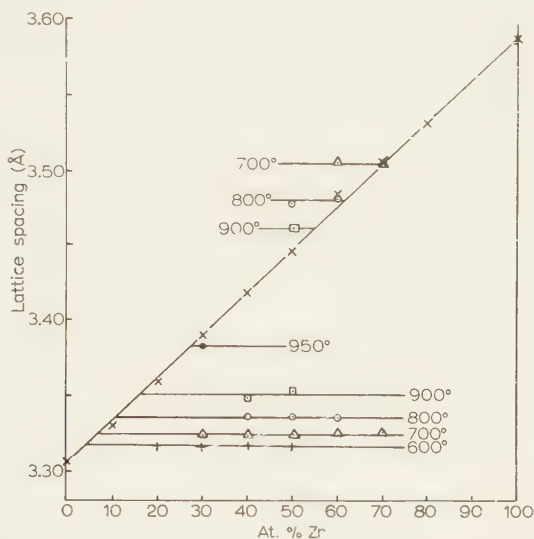


Fig. 5. Lattice spacings of body-centred-cubic niobium-zirconium alloys. $\times$, annealed in β ; $\bullet$ 950°C; $\square$ 900°C; $\circ$, 800°C; $\triangle$, 700°C; $+$ 500°C.

The present diagram is in good agreement with that given by ROGERS AND ATKINS¹⁰. The principal discrepancies are in the solid solubilities in niobium and α -zirconium. ROGERS AND ATKINS report solubilities of 13 at. % zirconium and 6.5 at. % niobium at the monotectoid temperature compared with 6% and < 1% in the present work.

OBSERVATIONS ON CERTAIN NIOBIUM AND TANTALUM SYSTEMS

Partial studies have been made of several binary systems of niobium or tantalum with rhenium and the platinum group metals. Information available from these studies and from previous work is collected in Fig. 6. The new data obtained on these systems is outlined below.

Niobium-ruthenium

A melting point survey showed a maximum in the liquidus of this system near 50 at. % ruthenium, and two minima at 1,680°C, 65 at. % ruthenium and 1,810°C, 40 at. % ruthenium. For an alloy containing 39 at. % ruthenium, a powder photograph revealed a body-centred-cubic phase only, suggesting a large solubility of ruthenium in niobium. GREENFIELD AND BECK²¹ have proposed that CsCl type ordering may be occurring in these alloys.

It is probable that the solid solubility of niobium in ruthenium is also high, an alloy of 34 at. % niobium showing an expanded hexagonal close packed pattern only.

The maximum near 50 at. % ruthenium probably corresponds with the tetragonal intermediate phase described by GREENFIELD AND BECK.

Niobium palladium

X-ray powder photographs of alloys of up to 50 at. % niobium showed a face-centred-cubic pattern only. The liquidus maximum near NbPd_3 may correspond with an ordered AuCu_3 phase, as reported by DWIGHT AND BECK¹¹ for the tantalum-iridium system, the absence of superlattice lines being due to the similar scattering factors for X-rays of niobium and palladium atoms.

GREENFIELD AND BECK²¹ reported a sigma phase in the niobium-palladium system. However, in the present work, no sigma structure was detected in alloys of 30-50 at. % palladium after arc melting, or after annealing at 1,000-1,200°C for 5-7 days.

Appreciable solid solubility of palladium in niobium exists, an alloy of 25 at. % palladium consisting of a single body-centred-cubic phase only.

Niobium-osmium

An X-ray survey of twenty alloys in this system showed considerable terminal solubilities, approximately 15 at. % in each component. The sigma phase exists from 30-54 at. % osmium and the χ phase over a range of about 10 at. % from 55-65 at. % osmium.

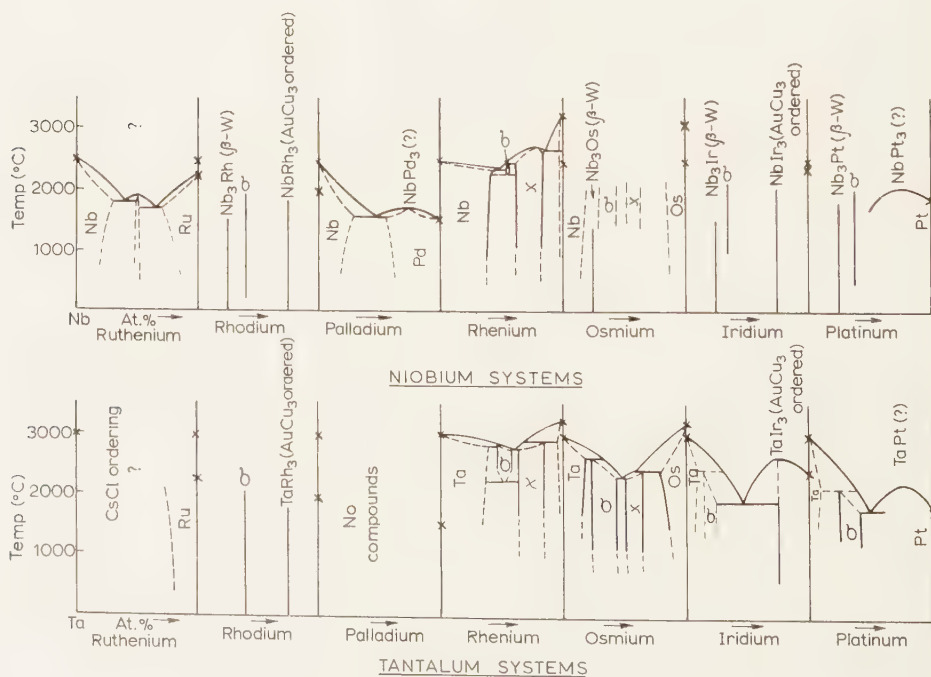


Fig. 6. Alloys with rhenium and the platinum metals.

Niobium-platinum

Observations on this system have been limited to liquidus determinations at the platinum end. The liquidus passes through a maximum near NbPt₃.

Tantalum-rhenium

The tentative diagram given in Fig. 6 is based on liquidus measurements and X-ray data on annealed alloys. The sigma phase is stable at temperatures of 2,200°C to the melting point, and exists from 47–60 at. % rhenium. The χ phase is stable at all temperatures, and exists over a wide homogeneity range of 61–86 at. % rhenium at. 2,200°C.

Tantalum-osmium

A tentative tantalum-osmium phase diagram is given in Fig. 6. It has been established by X-ray methods that:

- (1) Solid solubility of osmium in tantalum is 14 at. % at 2,200°C.
- (2) Two intermediate phases exist in the system: a σ phase and a χ phase.
- (3) The σ phase is stable from 1,200°C to the melting point and from 22–45 at. % osmium.
- (4) The χ phase is also stable at all temperatures up to the melting point. The maximum homogeneity range is 48–65 at. % osmium.
- (5) At 2,200°C, the terminal solubility of tantalum in osmium is 22 at. %.

Tantalum-iridium

Two intermediate phases have been previously reported in tantalum-iridium alloys, one with the σ structure and homogeneity range 75–85 at. % tantalum²², and the other an ordered AuCu₃ structure at TaIr₃¹¹. A liquidus survey suggests that σ is formed peritectically, and that TaIr₃ is a congruently melting phase.

Tantalum-platinum

The form of the tantalum-platinum phase diagram appears similar to the tantalum iridium system. A sigma phase exists over an appreciable homogeneity range²¹ and a liquidus maximum near TaPt₃.

CONCLUSIONS

It is apparent from Fig. 6 that many aspects of the alloy systems of niobium and tantalum with the later transition metals remain unexplored. However, the information available shows that the alloying behaviour of niobium with these metals parallels quite closely the corresponding tantalum alloys, both in the extent of the terminal solid solutions and in the intermediate phases formed. One noteworthy difference is in the phases with the β -tungsten structure formed in niobium systems with rhodium, osmium, iridium and platinum but which are absent in tantalum alloys. This difference has not been explained, but is probably associated with the relative stabilities of the sigma phases in niobium and tantalum alloys. The tantalum containing sigma phases exist over an extended homogeneity range, which embraces the composition where β -tungsten structures may be expected to form.

The solubility behaviour of niobium and tantalum in the second element also follows an interesting sequence. The solubilities in rhenium are low, about 2 at. %. The Group VIIIa elements, ruthenium and osmium, show much higher solubilities for niobium and tantalum. At iridium and rhodium, instead of a further solubility increase, AuCu_3 type ordered structures are formed, apparently congruently from the melt. In alloys with the Group VIIIc elements, rhodium and platinum, liquidus maxima also occur at the AB_3 compositions, but the phases responsible for these maxima have not been identified.

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ON THE FORMATION OF INTERMEDIATE PHASES IN ALLOYS OF Nb, Ta, Mo AND W WITH OTHER TRANSITION METALS

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SUMMARY

Certain phases found in transition metal alloys are described. The type of structure formed, and the manner in which the various atomic sites are occupied, is interpreted in terms of atomic size and valency effects.

INTRODUCTION

The complex crystallographic structures found in many alloys have been discussed by BOERDIJK¹ and by FRANK AND KASPER² in terms of the packing of spheres and the formation of triangulated coordination shells.

The simplest geometrical arrangements for the close packing of spherical atoms are the face-centred-cubic and close-packed hexagonal structures, and there are other ordered examples of these where only 12-fold coordination is found.

Many of the complex structures contain atoms with 12-fold coordination of the icosahedral type, together with other atoms of 14, 15 and 16-fold coordination. The size of an atomic site increases with the coordination number, and can be measured in terms of the mean interatomic distance or mean bond length associated with the site. Using this parameter, the formation of many of the complex structures can be understood. Ordering in many structures can be explained as the preference of a large atom to occupy a large atomic site and for a small atom to occupy a small site. The diameter of an atom can be obtained from the interatomic distance in the pure metal and this can be corrected to coordination number 12 using the criterion due to Goldschmidt.

Whilst many of the features of intermediate phases can be interpreted in terms of size effects, the body-centred-cubic metals of Groups V and VI show that in some cases the close-packing of spherical atoms does not provide a good basis for understanding a crystal structure, and that other effects can be important. The influence of these effects can be found in complex structures where the coordination shell for certain atomic sites suffers a large distortion from spherical symmetry.

The structures of several intermediate phases have been examined in terms of the coordination arrangements about the different atomic sites. It is shown that, for phases which consist mainly of atoms from Group VIII of the periodic table, the packing of hard spherical atoms is a useful concept.

For phases which consist mainly of atoms from Groups V and VI, the coordination shells of some of the atomic sites show large distortions from sphericity. It would appear that atoms from Group V and VI can tolerate such an environment.

β -W or A 15 structure

The structure is cubic with 8 atoms in the unit cell, and has two types of atomic sites:

Type I, 6 per unit cell with CN 14, and this forms the major skeleton. The characteristic feature of this skeleton is the formation of perpendicular chains of atoms in the lattice; the coordination of an atomic site being broken up into

2 at a distance of x ($x = a/2$)

8 at a distance of $1.23 x$

4 at a distance of $1.12 x$

Type II, 2 per unit cell with CN 12 (approximately icosahedral) all the neighbours being at $1.12 x$.

In the many known examples of this structure found in binary metallic systems, the atomic sizes of the two metals are approximately the same, the radius ratio lying in the range 0.91–1.08. Also, there is virtually no difference in volume of the atomic sites in the β -W structure, the average bond lengths being $1.17 x$ and $1.12 x$ for Type I and Type II sites respectively. However, the Type I atoms have a distance of closest approach along the chains 10–14% less than that found in the pure metals.

There is a marked stoichiometry of the β -W structure found in binary transition metal alloys about the composition A_3B , (LAVES³, HAWORTH AND HUME-ROTHERY⁴), and this can be taken as evidence of ordering between the two types of site. Moreover, the A atoms come from Group IV, V or VI, *i.e.* those transition metals which can have a *b.c.c.* modification. Thus it would appear that only transition metal atoms which can exist in a *b.c.c.* modification can suffer the large oblate distortion necessary for them to fit the Type I sites of the β -W structure.

 β -U or σ structure

The structure is tetragonal with 30 atoms in the unit cell. It consists of layers of atoms in a hexagonal type of arrangement, two layers per unit cell, with chains of atoms parallel to the *c* axis centering the open hexagons of these layers and situated between them.

There is some doubt about the exact atomic positions found in β -U (THEWLIS AND STEEPLE⁵, TUCKER⁶) in that a considerable "rumpling" of the hexagonal layers has been suggested. However, for the Fe–Cr system (BERGMAN AND SHOEMAKER⁷) and the Co–Cr system (KASPER⁸), X-ray data from single crystals has been interpreted in terms of flat hexagonal layers and straight perpendicular chains, with space group $D_{4h}^{14} - P 4/mnm$.

There are five types of atomic sites in this latter structure, as shown in Table I. The fourth and fifth columns are from the data of BERGMAN AND SHOEMAKER on the Fe–Cr σ phase: the values for mean bond lengths for the various atomic sites give a measure of the size of the different sites, while "maximum bond contraction" is a measure of the distortion from spherical symmetry and is defined as

$100 (\text{mean bond length} - \text{shortest bond length}) / \text{mean bond length}$.

There is a tendency towards prolate distortion in the Type II sites, whilst the Type V sites are oblate. Although the above calculations are made for Fe–Cr, the *c/a* ratios of the σ phases are constant to within 1%.

TABLE I
CONNECTIONS FOR THE σ STRUCTURE ATOMIC SITES

Type	No. per unit cell	C.N.	Mean bond length ($\text{\AA}$)	Max. bond contraction (%)
I	2	12	2.51	5.2
II	4	15	2.70	10.7
III	8	14	2.62	8.4
IV	8	12	2.52	5.5
V	8	14	2.64	14.0

C.N. = Coordination number

Evidence for ordering amongst the various types of atomic sites in the σ structure has been obtained from neutron and X-ray diffraction experiments (KASPER⁸). The measured ordering is shown in Table II — that for the systems Cr-Fe, Cr-Co and Mo-Fe is perhaps less well established than the others.

TABLE II
NUMBER OF A AND B ATOMS ON DIFFERENT ATOMIC SITES IN THE σ STRUCTURE

Type \ d_a/d_b	V-Ni		V-Fe		Cr-Fe		Cr-Co		Cr-Mn		Mo-Mn		Mo-Fe	
	2.71	2.49	2.71	2.54	2.57	2.54	2.57	2.50	2.57	2.70	2.80	2.70	2.80	2.54
	1.09		1.07		1.01		1.03		0.95		1.04		1.10	
I (2)	0	2	0.3	1.7	—	2	—	2	0	2	0	2	2	—
II (4)	4	0	4	0	4	—	4	—	1	3	4	0	4	—
III (8)	>6		>6		4	4	4	4	3	5	4	4	—	8
IV (8)		>7		>7	—	8	—	8	0	8	0	8	—	8
V (8)	>7		>6		4	4	4	4	4	4	4	4	8	0

The atomic diameters given in the table as d_a, d_b (corrected to a coordination number of 12), show that there is a good correlation between atomic size and lattice site, the largest atoms going to the largest sites and vice versa (except in the case of Mo-Fe, where the ordering data is not very certain).

Also sites I and IV are usually occupied by an atom from Group VII or VIII (elements which usually exist in a structure having a coordination number of 12) whilst atoms which are from Groups IV, V or VI (elements which have a *b.c.c.* allotrope) tend to go to the sites II, III and V. It is in these latter sites that the distortion is greatest and can be compared with that found in the β -W structure.

However, for all the known transition metal σ phases the diameter ratio varies between 1.01 and 1.16 and the occurrence of σ phase cannot be predicted.

Laves phases

There are three Laves phases which can be regarded as differing in the stacking of close-packed double layers of atoms. The stoichiometric composition of the structure is AB_2 , and the two types of atomic sites for *A* and *B* atoms have the same coordination in all three phases; there are small departures from the dimensions given below in the hexagonal phases, but for the MgCu_2 structure:

Site *A* (Mg atoms) has C.N. 16, 12 Cu atoms at a distance x and 4 Mg atoms at a

distance $1.05x$. It is an approximately spherical coordination site, with slight distortion ($+5\%$) in four tetrahedral directions.

Site B (Cu atoms) has C.N. 12, 6 Mg atoms at a distance x and 6 Cu atoms at a distance $0.86x$. It can be imagined as an oblate spheroid with an average bond length $0.93x$.

It is generally accepted that the Laves phases are "size factor" compounds. If the A and B atoms are thought of as hard spheres, then (in the cubic MgCu_2 modification at least) it is only for the radius ratio $r_A/r_B = 1.23$ that both $A-B$ and $B-B$ contacts can occur. This is then thought of as the "ideal" radius ratio for a Laves phase.

However, in arriving at this figure we have only used a coordination number of six for the B sites, since $B-A$ contact of hard spheres is forbidden by the geometry of the structure. Using the average bond lengths (calculated from coordination numbers 12 and 16) to establish a criterion for Laves phase formation, we find an "ideal" radius ratio of 1.09.

It might be expected that the preferred radius ratio will be between these two values, since anomalously short bond lengths in a given coordination shell will be more effective in determining the free energy of a phase than anomalously long ones; on the other hand it does not seem reasonable to use a C.N. 6 to decide the stability conditions for a phase in which high coordination numbers are characteristic.

If the radius ratios for the Nb, Ta, Mo and W-X_2 Laves phases (ELLIOTT AND ROSTOKER¹⁰) are examined (see Table III), the mean value is found to be 1.14, with values in the range 1.11 to 1.18. For the phases where Zr or Hf forms the A component, the mean value of the (Goldschmidt) radius ratio is 1.25, but in these cases there is a large contraction in the size of the Zr or Hf atoms when the Laves phase is formed (LAVES³). Thus the size of the Zr and Hf atoms is easily altered, and the above large value is not good evidence for the validity of the hard sphere packing "ideal" radius ratio of 1.23.

TABLE III
LAVES PHASES FORMED BY TRANSITION ELEMENTS

System	Type	r_A/r_B	System	Type	r_A/r_B
NbCr ₂	MgCu ₂	1.14	TaCr ₂	MgZn ₂	1.15
NbMn ₂	MgZn ₂	1.13	TaMn ₂	MgZn ₂	1.13
NbFe ₂	MgZn ₂	1.17	TaFe ₂	MgZn ₂	1.17
NbCo ₂	MgCu ₂	1.18	TaCo ₂	MgCu ₂	1.18
MoCr ₂	none	1.09	WCr ₂	none	1.10
MoMn ₂	none	1.07	WMn ₂	none	1.08
MoFe ₂	MgZn ₂	1.11	WFe ₂	MgZn ₂	1.12
MoCo ₂	none	1.11	WCo ₂	none	1.12

Ordered close-packed phases of C.N. 12, based on AB_3

There are several structures based upon close-packed layers ordered in one of two different ways and stacked in different sequences. Thus, in general, a radius ratio of 1.00 would be expected to favour the formation of such a structure.

Amongst the structures made up of ordered close-packed layers with hexagonal symmetry are:

cubic AuCu_3 -type, with stacking *abcabc*

hexagonal MgCd_3 -type, with stacking *abab*.

Another type of ordering in the close-packed layers (without hexagonal symmetry) gives a distorted AB_3 structure:

cubic $TiAl_3$ -type, and hexagonal $TiCu_3$ -type (SAITO AND BECK⁹). Ordered close-packed structures are found in transition metal alloys.

TABLE IV

ORDERED CLOSE-PACKED STRUCTURES FORMED BY TRANSITION ELEMENTS

System	Type	r_A/r_B	System	Type	r_A/r_B	System	Type	r_A/r_B
NbIr ₃	AuCu ₃	1.09	MoCo ₃	MgCd ₃	1.11	NbNi ₃	TiCu ₃	1.19
NbRh ₃	AuCu ₃	1.10	WC ₃	MgCd ₃	1.12	TaNi ₃	TiCu ₃	1.18
TaIr ₃	AuCu ₃	1.08				MoNi ₃	TiCu ₃	1.13
TaRh ₃	AuCu ₃	1.09						

The B component in all these phases normally exists in a close-packed allotropic form (from Group VIII of the periodic table). It would appear that the cubic AuCu₃ structure can only tolerate a size ratio of up to 1.10. If valency effects are constant, then for values slightly exceeding this the hexagonal MgCd₃ structure can be formed. For a ratio in the range 1.13-1.19 a different type of ordering in the close-packed plane can arise, leading to the distorted close-packed structure of TiCu₃.

Disordered close-packed phases

In many of the binary alloys of a Group V or VI element with one from Group VIII, extensive terminal solid solutions in the Group VIII element are formed, *i.e.* extensive *b.c.c.* or *h.c.p.* phase fields. In some cases an *h.c.p.* intermediate phase is found with c/a ratios slightly less than ideal.

TABLE V

SYSTEMS SHOWING DISORDERED CLOSE-PACKED PHASES

System	r_A/r_B	System	r_A/r_B
MoRh	1.04	W Rh	1.05
MoPd	1.02	W Ir	1.04
MoIr	1.04		
MoPt	1.01		

From Table V it can be seen that a necessary condition for their formation is that the atomic sizes of the two elements should be within about 5% of each other.

CONCLUSIONS

Concerning the intermediate phases found in transition metal alloys the following general rules seem to apply:

(1) β -W structure is an alternative to the *b.c.c.*, and can occur at a composition of A_3B where A is a metal normally having a *b.c.c.* structure. The radius ratio of the two elements must lie between 0.91 and 1.08, but it is suggested that the stability of the structure is associated with the electronic nature of Groups V and VI metals.

(2) β -U or σ structure in Nb, Ta, Mo and W transition metal alloys normally lies

between the stoichiometric compositions A_3B and AB_3 . Although some evidence for the effect of atomic size can be found (the radius ratio of elements which form this phase lies between 1.01 and 1.16), its occurrence cannot be predicted in terms of either size effects or electronic effects.

(3) Laves phases or ordered close-packed phases of $TiCu_3$ type are found if the radius is in the range 1.13–1.19. Laves phases or ordered close-packed phases of $MgCd_3$ type are found for the radius ratio between 1.11 and 1.13.

(4) $AuCu_3$ cubic superlattice can only exist for a radius ratio less than 1.10.

(5) Disordered close-packed phases (including extensive terminal solid solutions in the B component) can arise only with a small radius ratio (in the range 1.0–1.05 for Mo and W alloys).

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NITRIDES, CARBONITRIDES AND OXYNITRIDES OF NIOBIUM

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SUMMARY

Methods of preparing niobium nitrides and oxynitrides are described. The stability of the different phases have been thoroughly investigated. A survey of the carbonitrides of niobium is given and some of their properties are described.

NIOBIUM NITRIDES

CAUER AND JANDEK¹ and SCHÖNBERG² have recently published their reports on the niobium-nitrogen system. Their conclusions are in some respects contradictory and do not result in a clear description of the number and the relations of the phases in the system. We have therefore carried out a new systematic investigation in which we have paid particular attention to the purity of the starting materials, to the use of very exact and reproducible methods of preparation, and to a very good analytical characterisation of our products.

Experimental procedure

The metal powders were prepared in a vacuum furnace under a pressure of 10⁻³ mm Hg in an atmosphere of nitrogen or ammonia. The metal powder used was of commercial grade niobium (99.79% Nb)*; a powder with less impurities was prepared by filing niobium rods with 99.99% Nb until the powder passed a sieve with 6400 mesh/cm². The niobium hydride** was in the form of a very fine powder with 95.96% Nb, 0.99% H.

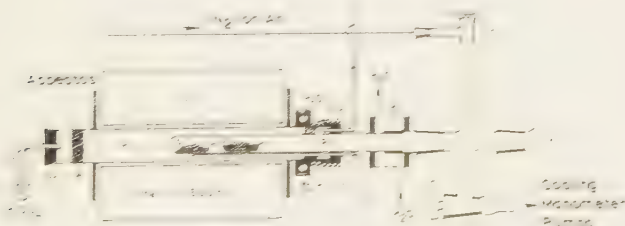


Fig. 1. Apparatus for nitriding metal powders.

*Armco Metallurgical Corp., Chicago.
 **Metal Hydrides Inc., Beverly.

and some impurities of O, N and C. For the synthesis of the nitrides we used alumina boats filled with the niobium metal or the niobium hydride. The boats were placed inside a horizontal ceramic (pythagorasmasse) tube, which was electrically heated. In some cases we used a facility which is shown in Fig. 1 and which was preferred in experiments where there was no change of the nitrogen atmosphere. The reaction tube was surrounded by a slightly wider tube through which we conducted a stream of very pure nitrogen or argon. This procedure prevented any diffusion of air into the reaction tube, and we could be sure that our preparation was not spoilt. In other cases we used a reaction tube, open at both ends, and a continuous stream of the nitriding gas.

Nitrogen and argon were carefully purified by passing them over finely divided heated copper, kieselgel and phosphorus pentoxide to remove traces of oxygen and moisture. A further purification of argon was obtained by leading the gas over heated magnesium and titanium to remove traces of nitrogen. The ammonia was completely dried by metallic sodium.

We have found six phases in the system in question, which we called α , β , γ , δ , δ' and ε . Some were already known. α is the metallic phase (body-centred-cubic), β is the hexagonal phase of interstitial Hägg type corresponding closely to the formula Nb_2N , and δ is the face-centred-cubic phase that has approximately the formula NbN . The γ -phase has a composition near $\text{NbN}_{0.75}$ or Nb_4N_3 , and a crystal lattice that can be derived from the NaCl type lattice of the δ -phase by removing one fourth of the nitrogen atoms. The nitrogen deficiency results in a distortion of the cubic lattice to tetragonal symmetry with a ratio $c/a = 0.97$. The δ' - and ε -phases are hexagonal with compositions very close to NbN . Their lattices have an identical arrangement of the nitrogen atoms in a primitive hexagonal cell but are distinguished by a different sequence of the niobium atom layers in the c direction: δ' has the anti-nickel arsenide type sequence $ABAB \dots$, whereas ε has the sequence $AABBAABB \dots$. Fig. 2 shows the structures of the phases in the niobium–nitrogen system.

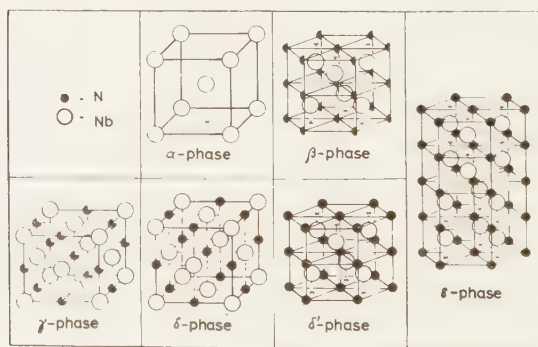


Fig. 2. Crystal structures of the phases found in the niobium–nitrogen system.

We suppose that the thermal stability and the rate of formation of the different niobium nitrides are very similar. During the reaction of niobium metal or niobium hydride with nitrogen or ammonia between 800 and 1,500°C the product generally consists of several compounds and the observations are somewhat confusing. Equi-

equilibrium is obtained only after a rather long time. By observing many experiments under slightly different conditions it was possible to decide the relationships of the different phases. In Fig. 3 we give a tentative phase diagram for the niobium-nitrogen system.

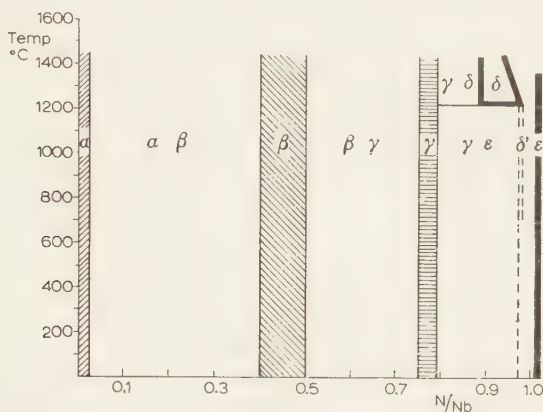


Fig. 3. Phase diagram of the system niobium-nitrogen.

The α -phase undoubtedly has a definite homogeneity range which depends in some way on the temperature. However, we did not try to determine exactly the solubility of nitrogen in niobium. The β -phase extends, at a temperature of 1,200–1,400°C, between the compositions $\text{NbN}_{0.40}$ and $\text{NbN}_{0.50}$. We observed only a small shift in the lattice constant c from 4.954 Å for $\text{NbN}_{0.40}$ to 4.995 Å for $\text{NbN}_{0.50}$. The variation of the homogeneity range at different temperatures was negligible. The γ -phase has a small homogeneity range from $\text{NbN}_{0.75}$ to $\text{NbN}_{0.79}$ and only a small variation of its lattice constant c from 3.311 to 3.335 Å.

Whilst the α , β and γ -phases are stable over the whole range of our experimental temperatures (*i.e.* room temperature to 1,500°C), the δ , δ' and ϵ -phases undergo phase transformations at more or less definite temperatures. The δ' -phase seems to be unstable at any temperature. It appears only during the formation or transformation of other stable nitrides and disappears directly afterwards. Therefore we cannot exactly determine its phase boundaries. But it is quite sure that it has a composition in the neighbourhood of NbN . The cubic δ -phase is stable only above 1,230°C. At lower temperatures it transforms into the δ' -phase. At relatively low nitrogen pressures (*e.g.* in vacuum) this δ' -phase loses nitrogen resulting in the γ -phase; at nitrogen pressures of about 760 mm mercury it is transformed into the ϵ -phase. By increasing the temperature above 1,230°C the δ - and γ -phases can be transformed into one another by adding or removing nitrogen, which is easily done by varying the pressure. The homogeneity range of the cubic δ -nitride extends from $\text{NbN}_{0.88}$ to $\text{NbN}_{0.98}$. The exact composition depends on the nitrogen pressure. The lattice constant $a = 4.382$ Å for $\text{NbN}_{0.88}$ increases to $a = 4.392$ Å for $\text{NbN}_{0.98}$. The ϵ -phase exists only at temperatures below 1,370°C in the composition range $\text{NbN}_{1.000}$ to $\text{NbN}_{1.018}$. Above 1,370°C it loses some nitrogen and is transformed into the δ -nitride. The ratio $\text{N}:\text{Nb} > 1$ indicates that the ϵ -phase has a defect lattice with niobium vacancies. The deviations

from the ideal formula NbN are so small, however, that this assumption cannot be proved by density measurements. Fig. 4 represents a scheme of the possible transformations of the higher niobium nitride phases and the experimental conditions for these transformations. The transformations along the full lines are easily reproducible, but the transformations along the dotted lines are not always observed.

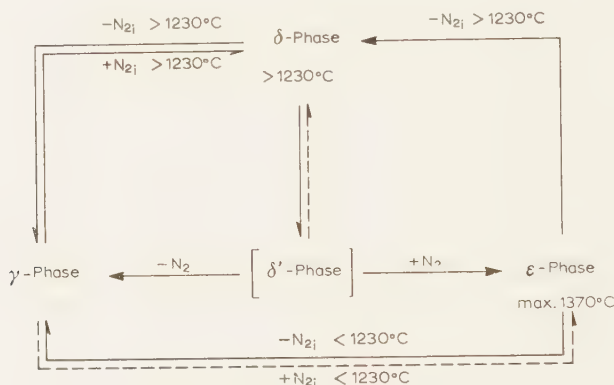


Fig. 4. Transformations of niobium nitrides.

NIOBIUM OXYNITRIDES

Different authors^{1,2,3,4} have proposed the existence of niobium oxynitrides. We have investigated systematically the Nb–NbO–NbN section of the ternary system Nb–O–N (Fig. 5) because one would expect oxynitrides to form preferentially in this region. The oxynitrides were synthesized from powdered mixtures of niobium metal, niobium monoxide NbO, and the cubic niobium nitride (δ -NbN) at temperatures between 1,200 and 1,450°C in an atmosphere of nitrogen or argon or *in vacuo*. Reaction was sufficiently fast under these conditions.

We expected the formation of a ternary mixed crystal from the two related cubic phases NbO and δ -NbN; the former has the structure of highly (25%) disordered

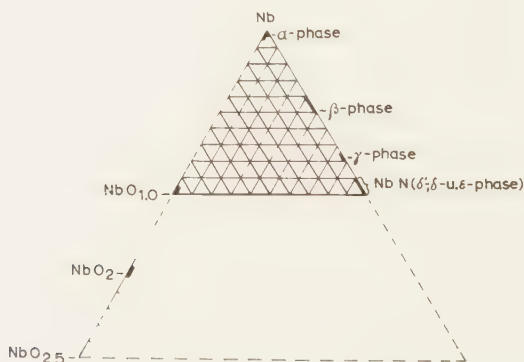


Fig. 5. Part section of the ternary system niobium–nitrogen–oxygen.

rocksalt and the latter is of the same type but only slightly disordered (Fig. 6). We never found, however, such a mixed crystal. We always found mixtures of NbO_2 and niobium nitrides. The structure of the latter phase depended on the experimental conditions: $\delta\text{-NbN}$ was formed in an atmosphere of nitrogen, and δ - and β -nitrides

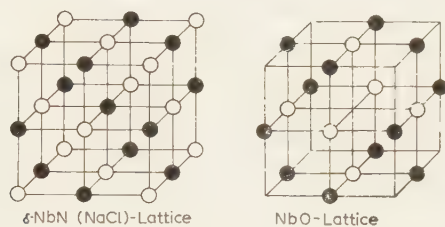
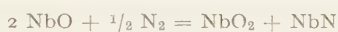


Fig. 6. Crystal structures of $\delta\text{-NbN}$ and NbO .

were formed *in vacuo*. The formation of NbO_2 is surprising since NbO is normally very stable and was never observed to disproportionate into Nb and NbO_2 . One has to conclude that NbO in nitrogen atmosphere reacts with nitrogen following the equation



in vacuo NbO reacts with NbN following the equation



No real ternary phases were observed at temperatures between 1,200 and 1,500°C if one excludes a small solubility of oxygen in the δ -nitride up to the composition

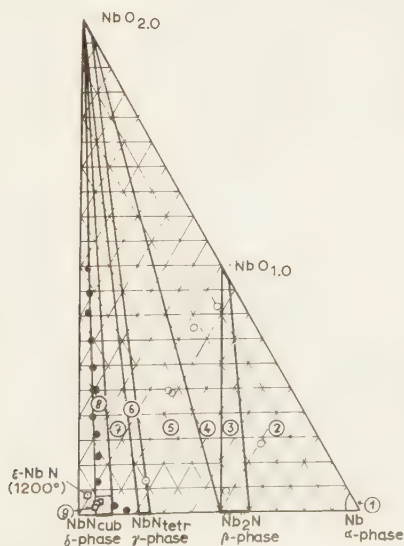


Fig. 7. Part section of the ternary system niobium-nitrogen-oxygen.

$\text{NbN}_{0.90}\text{O}_{0.05}$. In all other cases the pure nitride phases are in equilibrium with the pure oxides NbO and NbO_2 , respectively, as shown in Fig. 7.

Contrary to these not very positive results about the formation of mixed crystals between niobium nitrides and oxides we found that real oxynitrides can be prepared at temperatures as low as 750°C by passing ammonia over niobium pentoxide. The ammonia behaves simultaneously as a reducing and a nitriding agent. The reaction leads to the formation of two phases we propose to call $\delta\text{-Nb}(\text{O}, \text{N})$ and $\varepsilon\text{-Nb}(\text{O}, \text{N})$, according to their crystal structures which correspond to the δ - and ε -phase in the Nb-N-system.

The $\delta\text{-Nb}(\text{O}, \text{N})$ -phase has a cubic lattice like the $\delta\text{-NbN}$, but with a smaller lattice constant of $4.33 \text{ \AA}$. It has a brass-like colour and a good electric conductivity. From the chemical analysis one gets the formula $\text{NbN}_{1.08}\text{O}_{0.35}$ with some deviations for the different samples. The density measurement, however, proved this phase to be of lower density than was expected from the formula given above. The observed density agrees much better with $\text{Nb}_{0.69}\text{N}_{0.75}\text{O}_{0.25}$ and we believe therefore that the $\delta\text{-Nb}(\text{O}, \text{N})$ -phase has a metal-deficient rocksalt lattice with a random distribution of N and O over the entirely filled nonmetal positions and with only partly occupied metal positions.

The $\varepsilon\text{-Nb}(\text{O}, \text{N})$ -phase is greyish black and has a hexagonal lattice like $\varepsilon\text{-NbN}$. The X-ray patterns of this oxynitride show some very diffuse lines as substances do which have an appreciable amount of stacking disorder in the lattice. It follows from the chemical analysis and the observed density that the $\varepsilon\text{-Nb}(\text{O}, \text{N})$ -phase must be described by a formula about $\text{Nb}_{0.82}\text{N}_{0.81}\text{O}_{0.19}$. The two oxynitrides are stable only at low temperatures up to about 900°C . Above this temperature they decompose to niobium oxides and simple binary niobium nitrides.

Recently KIESSLING and PETERSON⁵ found analogous oxynitrides of tungsten with formulae like $\text{W}_x\text{N}_y\text{O}_{1-y}$ with $x \approx y \approx 0.62$ and a cubic face-centred structure.

NIOBIUM CARBONITRIDES

We synthesized various niobium carbonitrides with compositions between Nb, NbC and NbN by heating binary niobium carbides in nitrogen atmosphere at $1,250$ to $1,450^\circ\text{C}$. The carbides were prepared from pure niobium metal and soot at about

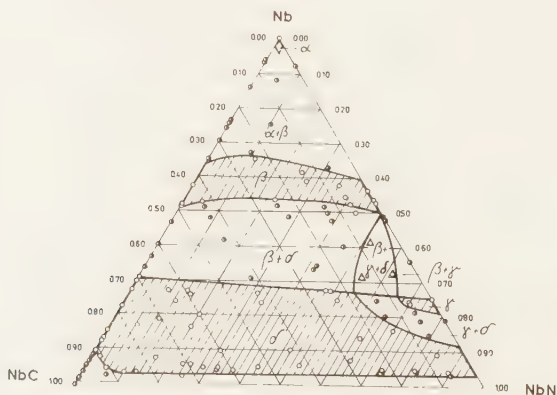


Fig. 8. Section of the ternary system Nb-NbC-NbN.

2,000°C. The carbonitride samples were analysed chemically and characterized by X-ray methods. The results⁶ enabled us to construct the ternary system Nb-NbC-NbN which is shown in Fig. 8. The binary systems Nb-C and Nb-N both contain a hexagonal β -phase and a cubic δ -phase. As can be seen from Fig. 8, there is a complete substitution of carbon and nitrogen in corresponding phases. The broad homogeneity ranges of the phases are maintained. The variation of the lattice constants in these extended homogeneous regions depends on the ratio C : N and Nb : (C + N). A complication is introduced by the tetragonal γ -nitride. This phase dissolves some carbon but does not extend appreciably into the system. It causes, however, a region of three coexisting phases $\delta + \gamma + \beta$.

The solubility of the nonmetals in the metal phase (α) seems to increase, if carbon and nitrogen are both present, compared with the simple binary systems. The nitride phases δ' and ϵ cannot occur in our diagram for they are not stable at the temperatures used.

At the pressure of 760 mm, which was the maximum used in our experiments, the phase boundary from the binary compound with maximum carbon content NbC_{0.92} to the compound with maximum nitrogen content NbN_{0.98} never reaches the straight line representing the ratio (C + N) : Nb = 1. This may be possible, however, by using higher pressures. Our phase diagram is not complete, of course, since the influence of nitrogen pressure was not considered, but it may be used as a good approximation for many purposes.

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THE PHASE CONSTITUTIONS OF SOME NIOBIUM-BEARING AND ASSOCIATED TRANSITION METAL SYSTEMS

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SUMMARY

A constitutional survey is given of niobium-bearing ternary systems, several of which have been determined, and the underlying principles are discussed in some of their broader aspects. The systems represent substantially solid-solution and compound-controlled types. Miscibility bay formation is an important variant to the first, implying coherent segregation effects and strain-hardenableity. The second can exhibit some complex phase assemblies and new compounds; although brittle, alloys here may still yield valuable properties like oxidation resistance. Fundamentally niobium systems are viewed only as part of the surrounding transition metal unity in the periodic table, and non-equilibrium states obtain a special practical significance.

INTRODUCTION

It is intended in this account to attempt a survey of certain ternary transition metal systems grouped around niobium, though not necessarily all containing this metal, because from the fundamental aspect niobium is not particularly unique: it participates in a broader pattern, in which all Group IV–VIII transition metals should be considered as a whole. To illustrate this essential unity, six ternary diagrams (Fe–Cr–Mo, Fe–Cr–W, Co–Cr–Mo, Co–Cr–W, Ni–Cr–Mo, Ni–Cr–W¹) which, in conjunction, bring out many basic points, are reproduced in Fig. 1 as an example; these are discussed in detail elsewhere, but some features relevant in the present context are: (a) the consistent stabilisation of σ -phase by molybdenum, and its inhibition in favour of ξ -phase by tungsten; (b) the prevalence and limitation of atomic size and of electron structure as determining factors; (c) the variability of effective “valencies” of the parent metals with alloy proportion and heat-treatment; (d) the delineation of areas of embrittlement and of precipitation hardenableity, and thus of potentially useful alloy fields.

Ternary diagrams mainly will be considered. For details of the Nb-base binary systems, reference should be made to recent publications². The small amount of published work on Nb-bearing ternary systems will be referred to below together with the present investigations.

From atomic size and electron considerations, the following broad classes of Nb-base ternary systems should be distinguished: (1) those permitting solid solutions; (2) those favouring inter-transition metal compound formation; and (3) those in which valency and electron compounds such as aluminides and silicides prevail, leading on to (4):

systems with largely interstitial compounds such as niobium carbides, nitrides, borides, and oxides. Overlapping stages between these groups clearly exist, and these entail, in practice, some of the most important properties.

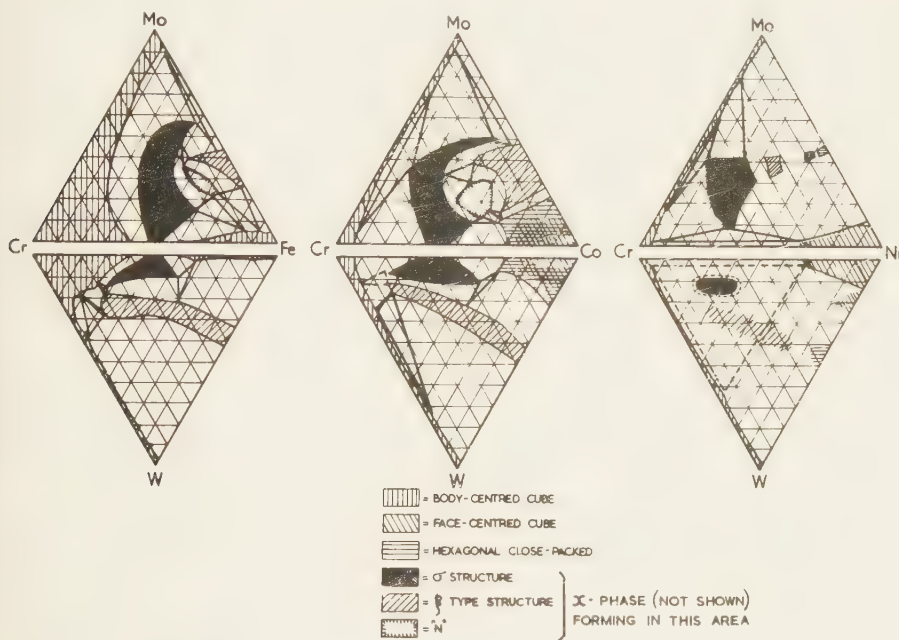


Fig. 1. Ternary diagrams of Fe, Co and Ni with Cr–Mo and Cr–W. Joint presentation, for illustration (600°C equilibria, but in some areas only approached).

Equilibrium, however, is only the target of all reaction, and in the present refractory transition metal alloys, the kinetics towards it are of a very special significance, since non-equilibrium systems often tend to be persistent. Fundamentally, the following, perhaps rather unorthodox viewpoint may be suggested: to regard the *pure* transition elements merely as not very distinctive members (or transitory “stations”) in a chain of states, in which each of their mutual alloy states is an almost equally important member. This is supported by the very nature of the transition metal in having incompleting inner electron orbitals, so that “alloying” substantially fills or depletes these orbitals, in a process, in which each alloy condition may be considered as possessing a near-elemental character. There are obvious reservations to this theme, for instance towards the end of the long periods where a very stable electron configuration is approached and can be attained by losing or gaining a few electrons; however, the concept proves useful in many types of problem, such as in diffusion. For example, in a niobium–molybdenum alloy solid solution there would be, at each stage of formation through diffusion, a progressive interchange of electrons between Nb and Mo atoms to give fractional filling or depletion of 3d orbitals and, in PAULING’s sense, a change of effective valency. Thus, in a Nb/Mo diffusion couple, each transitory pair of solid solutions approaching one another in composition can be considered as if they were two new elements, replacing Nb and Mo as primaries. The consequence is that, from this new couple, different metastable phases may arise, which, though

foreign to the given system when in equilibrium, can represent known equilibrium phases in related systems. Thus in the Fe–Cr system, manganese-type structures may occur metastably during diffusion and the σ phase appear at other than its equilibrium temperatures³. If we consider a system which has not Fe and Cr but two partial [Fe $\rightarrow$ Cr] and [Cr $\rightarrow$ Fe] solid solutions as its terminal members, these can be electronically much more akin to manganese (the element between Fe and Cr) than to either Fe or Cr and quasi-elemental also in this sense. (Note also the close structural, and constitutional relations between the brittle σ -FeCr and the α - and β -Mn phases; furthermore, a metastable face-centred cubic state observed during diffusion Fe $\rightarrow$ $\leftarrow$ Cr is indeed better regarded as one equivalent to γ -Mn rather than to the Fe–Cr γ -loop). Similarly, transient *lattice-spacings* may arise in a solid solution series during diffusion, which indicate quasi-elemental intermediate stages. These points are mentioned here, because they introduce aspects to be exemplified below.

SOLID SOLUTION AND MISCIBILITY BAY SYSTEMS

Points of principle

Fig. 2 shows a survey of ternary niobium-based transition metal systems, hypothetical, but predictable from existing knowledge (Nb = top corners). It represents

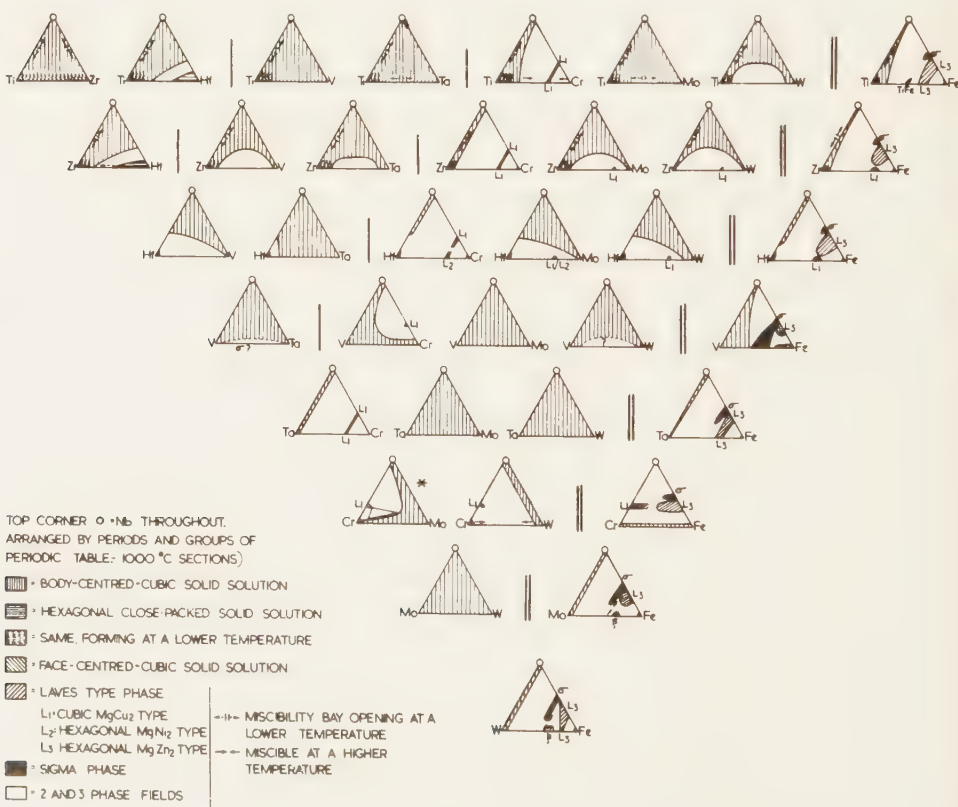


Fig. 2. Niobium-base ternary transition metal systems, as predictable from known binaries.

* = As determined. - 1,000°C sections.

the 1,000°C sections, with an indication, however, for higher and lower temperatures, if different. The sequence runs from Group IV $\rightarrow$ V $\rightarrow$ VI, but one Group VIII metal (Fe) is also included to typify the further constitutional trend along the First Long Period.

Miscibility bays within primary solid solution fields are a major feature; their occurrence and extent is principally determined by atomic size, the apices facing the metal intermediate in atomic diameter. The implication is that, starting from a continuous binary series of solutions, third element addition would introduce graded age-hardenability, which may become effective through (a) a slight composition advance or (b) a temperature decrease: the latter because the extent of the bay generally increases with decreasing temperature.

Quenches and carefully controlled anneals provide a means of introducing precipitates of a variety of types, either in composition bands continuous with the matrix, or as distinct heterogeneous isomorphs at opposite ends of tie-lines. They are liable to form as coherent strain-producing lattice lamellae, of modulated structure and concentration. This type of dissociation of a single BCC (body-centred cube) into two implies "uphill diffusion" effects of the kind known for face-centred cubic metals from DANIEL'S work⁴ on Fe-Cu-Ni alloys; the rate of such diffusion and character of the segregate can be critically adjusted by choice of time/temperature and composition variables.

A further type of precipitation able to superimpose on this, is that of Laves phase, *i.e.* a true intermetallic compound, which will form by a more normal nucleation-and-growth process. However, the processes are closely interconnected, because the relation between the BCC parent and Laves phase structure permits easy transformation of lattice islands, once, compositionally, this has become favourable; it may further be aided by the concurrent isomorphous matrix dissociation. Indeed, it is interesting to note that formation of both BCC miscibility bay and Laves structure (AB_2) are conditional on similar atomic diameter ratios $d_A : d_B \approx 1 : 1.2$; this well known condition favouring Laves phases is the same as that for the *A* and *B* atoms being mutually soluble in a third transition metal of intermediate size.

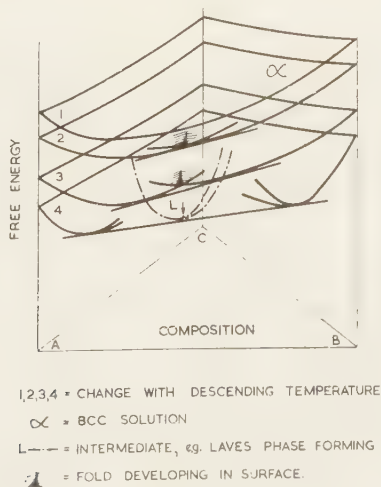


Fig. 3. Free energy stages in ternary miscibility bay formation.

In terms of *free energy*, the position may be presented as in Fig. 3: on approaching the bay limit (whether with temperature or composition), the free energy curves begin to intersect at so small an angle that an effectual "smearing" can occur on either side, and the compositions of the coexisting phases become uncertain. Experimentally, therefore, reaction is here so sluggish that boundary determination becomes imprecise, even in principle. Yet, for alloy development, these critical areas are probably some of the most important ones. It means that even within ostensibly single-phase fields pre-precipitation and uphill diffusion effects can occur *incipiently* on an atomic scale, even extending to the binary sides, although the latter may have been previously accepted as continuous solid solutions. (Possible examples: Nb–V and Mo–Cr, where the atomic diameter differences, though well within Hume-Rothery's favourable "15% zone" — 7.5 and 8.5% — compare with 8.8, 6.8 and 9.2% for Zr–Nb, U–Nb, and W–Cr, where miscibility bays *are* formed.) The possibility of latent low-temperature bays in such apparent continuous solution systems cannot be ignored; though equilibrated only after prohibitive times, their existence can still directly influence reaction kinetics and physical properties. Also, the diffusion rates from the primary elements, *e.g.* on sintering, would be affected.

Specific work

Examples of ternary systems with miscibility bays are self-explanatory from Fig. 2. As far as the writer is aware, past work has dealt with only the following systems:

Nb–Ta–Mo, Nb–Ta–W, Nb–Mo–W⁵: Complete solid solutions reported.

Nb–Ta–Zr (Zr-corner)⁶: Solid solutions of Nb and Ta in β -Zr; eutectoid decomposition $\beta \rightleftharpoons \alpha\text{-Zr} + \beta$ (Ta-rich).

Nb–Ti–Mo (Ti-corner)⁷: Solid solutions of Nb and Mo in β -Ti; eutectoid decomposition $\beta \rightleftharpoons \alpha\text{-Ti} + \beta$ (Mo-rich).

None of this work seems substantially to deal with the miscibility bay question, or with higher Nb alloys. We have investigated, as being a typical ternary system of this kind, the complete system Nb–Cr–Mo by X-ray analysis (1,000°C section, but some aspects at other temperatures). The resulting diagram closely bears out



Fig. 4. Alloy 10% Nb, 60% Mo, 30% Cr(atomic), annealed 1,000°C, 14 days. ($\times 600$)

Fig. 2 (sketch marked by asterisk). A detailed report will be given elsewhere, but the following points are here relevant.

As predicted, a miscibility bay occurs, with apex towards Mo, the single phase BCC α field dividing into duplex ($\alpha_1 + \alpha_2$). Laves phase (L) enters the assembly as a third constituent in defined areas, involving ($\alpha_1 + L$), ($\alpha_2 + L$) and ($\alpha_1 + \alpha_2 + L$) fields. With decreasing temperature the bay becomes more extensive, the resulting two daughter phases being of larger and smaller lattice spacing than the parent. Intermediate spacing changes can be produced by annealing a given quenched alloy under varying temperature/time conditions, a process associated with marked strain-ageing effects, and a hardness maximum. Hardening can occur by ($\alpha_1 + \alpha_2$) and/or by L nucleation, so that a considerable variety of intermediate stages arise, some very sluggish in developing. Fig. 4 shows clearly a network of lamellar micro-segregates formed along crystallographic planes of the parent crystal; the precipitate is here the Cr-enriched, and the matrix the (Mo, Nb)-enriched phase; the variation of orientation from crystallite to crystallite may be noted. The alloy had been single phase and homogeneous previous to the 1,000°C anneal.

Tie lines in Nb-Cr-Mo could be readily located, and, within the single α field, spacing contours follow, for the most, the general direction prescribed by known atomic sizes; however, a pronounced swing occurs adjoining the Cr-Mo side. This is believed to be of special significance, and is discussed in the next section. The relative widths of the α_{Cr} and α_{Nb} "arms" well reflect the atomic size differences Mo/Cr (8.5%) and Mo/Nb (5.0%).

The cubic Laves phase in this system, Cr₂Nb, is typical of the alternative mode of stacking during precipitation referred to further in a later section.

Other features examined on the Cr-Nb-Mo alloys were melting point and oxidation resistance; a survey of the latter property shows systematic, and in certain areas very promising, improvements compared with Nb (dealt with elsewhere). Combining this effect with that of age-hardenability, areas for developing useful Nb- and Mo-base alloys seem to emerge clearly, and are worth pursuing by fourth element additions.

Reverting to Fig. 2, Group IV metal addition to Nb introduces the further factor of low temperature eutectoid BCC $\rightarrow$ HCP transformation of $\beta \rightarrow \alpha$ -Ti type. It is operative below about 800°C, and, owing to restricted solubility, is liable to occur for quite moderate Ti, Zr, or Hf contents. Group VI metal additions, on the other hand, promote the ternary bays for W and Mo, degenerating into Laves phase stacking for Cr; this leads, in the sequence Mn $\rightarrow$ Fe $\rightarrow$ Co $\rightarrow$ Ni, to enhanced compound and superlattice formation (see later section). Interplay of all these factors by balanced ternary or quaternary additions to Nb clearly presents an attractive basis for niobium alloy development, which in fact has since been applied with some success (R. SMITH, this Symposium).

PRE-EQUILIBRIUM STATES

The following two examples are given to illustrate the pre-equilibrium conditions referred to in the Introduction.

(a) *A complete solid solution system: Cr-Mo*

During an X-ray study on the interdiffusion of pure chromium and molybdenum metals, using elemental powders of fine particle size, intimately mixed and compacted

in varying proportions, a sequence of intermediate states was obtained, as shown in Fig. 5. The final equilibrium curve⁸ is here approached in two diffusion stages, and lattice-dimensions of the partial solution phases are used as a measure of approach.

The point to be brought out in Fig. 5 is the progressive lag in equilibration towards central compositions, translatable to an intermediary "apparent" phase diagram, as shown inset. A *transient* miscibility bay results, which is extraordinarily akin to *stable* ones in other, related, systems: particularly that in Cr–W⁹ (see e.g. HANSEN ref. 2, p. 571). This Cr–W bay may well be regarded as an evolution of that in Cr–Mo; but whilst in Cr–W we have actual *uphill* diffusion (below 1,500°C), in Cr–Mo this remains *downhill* throughout, but verges on the critical free energy conditions of Fig. 3.* The addition of *niobium* to Cr–Mo (Fig. 2) operates in causing actual immiscibility, and is a factor equivalent to descending temperature or diffusion rate on the binary side. The swing of ternary Cr–Mo–Nb tie-lines adjoining Cr–Mo supports the same close interrelation.

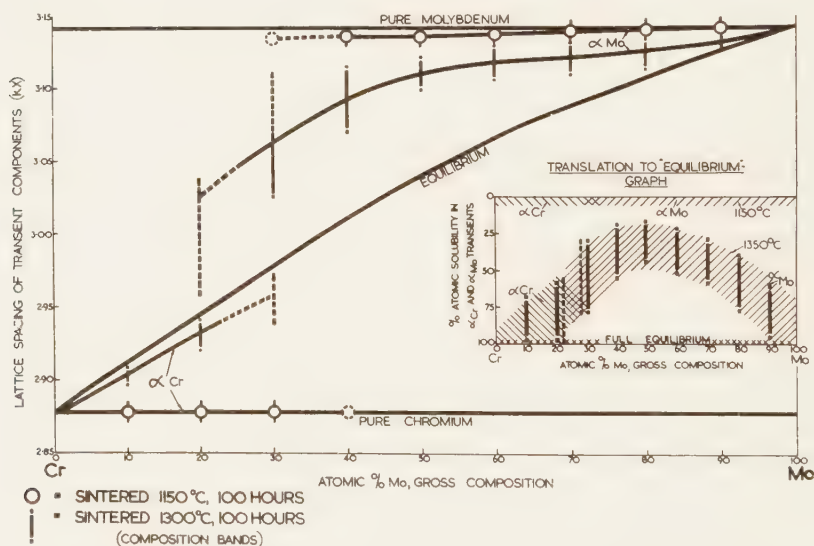
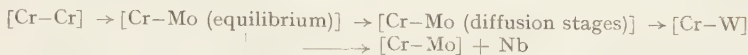


Fig. 5. Diffusion progress in Cr–Mo powder compacts, in terms of lattice spacings observed. Inset: Translation to "transient" phase diagram.

The slight positive deviation from Vegard's Law for the Cr–Mo (equilibrium) spacing curve, see Fig. 5, almost suggestively appears as a "remnant" of the major convexity observed during diffusion progress. This would indeed link well with the accepted viewpoint of solid solutions as involving localised deviations from average lattice dimensions, in which the ratio of solute/solvent atoms (here Cr/Mo) may fluctuate over small lattice regions. The coarser-scale segregates occurring amongst particles during interdiffusion would appear as a stage in the same process-sequence, terminating in this slight permanent convexity.

* It may be asked whether in Cr–Mo a true miscibility bay may not actually be latent at lower temperatures; or, in contrast, whether in Cr–W the true bay extends as high as observed: complete solid solution only having been too sluggish in attainment.

Since Cr and Mo are equi-valent, atomic size will here be the dominant factor, which makes the series:



fundamentally simple and attractive for study.

g) An intermetallic compound system: Fe-Mo

The binary diagram Fe–Mo may stand as typical, in the present context, for a compound-bearing system: It contains two restricted BCC terminal solid solutions α_{Fe} and α_{Mo} , and two intermetallic phases, $\xi = \text{Fe}_7\text{Mo}_6$ ¹⁰ and $\sigma = \text{FeMo}$ ¹¹, the former being stable at all temperatures to melting point, the latter only between 1180° and 1540°C. (See diagram: HANSEN, ref. 2, p. 669).

The progress towards this equilibrium has been studied in a series of diffusion experiments, using pure iron and molybdenum powder mixtures in varying proportions and reacting at varying temperatures (500 to 1,400°C) for varying times. Successive changes in constitution and in primary lattice spacings were followed. A full account is here not possible, but the relevant results are summarised in Table I.

The essence is that approach to equilibrium proceeds by way of transient states, both in regard to solid solutions and compounds formed, which are not necessarily innate to equilibrium in the given system. A transient "N" phase occurs, identical with the ternary compound N met in previous work on the Fe-Mo-Cr and Co-Mo-Cr¹ systems (see Fig. 1). Thus a structure which, when stable, is found in these ternary alloys appears en passant during diffusion in the binary Fe-Mo assembly. Both the

TABLE I
STRUCTURAL CHANGES DURING Fe-Mo DIFFUSION

Temperature	Constitution and lattice spacings
500°C	$\alpha_{\text{Fe}} + \alpha_{\text{Mo}}$, coexist throughout. No reaction, shown by spacing constancy at Fe and Mo values, with time.
800°C	α_{Fe} and α_{Mo} persist up to 15 hours, giving after 100 hours: Intermetallic Compound + α_{Fe} or α_{Mo} (depending on composition). α_{Fe} lattice expands with time, showing Mo solution to about 3% after 15 hours, about 6% Mo after 100 hours. α_{Mo} hardly yet contracts, but about 0.8% Fe in solution are indicated after 100 hours. A new intermediary phase (not ξ or σ) appears near Fe-end, increasing with time; with increasing Mo, this yields first to N type phase then to ξ (equilibrium).
1,100°C	α_{Fe} lattice expands to a spacing value indicating supersaturation up to approx. 18% Mo in Fe lattice; equilibrium corresponds to 9% Mo only. α_{Mo} contracts: up to 4% Fe in solution; the reported equilibrium value is 4% Fe. ξ phase immediately appears at all compositions. Equilibrium nearly attained throughout, apart from some remaining α_{Fe} supersaturation.
1,400°C	(Within σ stability region): Some $\alpha_{\text{Fe}} + \alpha_{\text{Mo}}$ coexist now where they did not at 1,100°C. Maximum solution in α_{Fe} about 18% Mo, near equilibrium value of 22% (?). α_{Mo} contracted, indicating up to 13% Fe in solution (equilibrium about 11% Fe). A transient N phase appears (known previously as ternary Fe-Mo-Cr compound), and a further (N') phase.

All compositions are in *atomic* %.

N and N' phases are closely related and of the σ -type, though distinct and intermediate to ξ and σ .

Furthermore, the coexistence of primary α_{Fe} and α_{Mo} solid solutions (impossible in equilibrium) can be metastably preserved to considerable times and/or high temperatures and a pronounced supersaturation of Mo in α_{Fe} occur, manifested by transiently excessive lattice expansion and at the cost of some retardation in compound formation. This again links with the free energy relations discussed before and suggests a potential α - α miscibility, "cut off" as it were, in Fe-Mo by liquid formation, but realisable by third metal addition, e.g. of Cr (a mutual solute in both Fe and Mo). In Fe-Cr and Fe-Mo the formation of either σ or ξ is associated with the opening of the α solution bay (whether complete or cut-off), and the structural characteristic of the σ -phase in being descendent from BCC parents is maintained.

Considering the ternary miscibility bay formation (as in the section SOLID SOLUTION AND MISCIBILITY SYSTEMS) this strongly suggests the existence of "pseudo-miscibility bays", in that the nucleation effects associated with truly stable bays (modulated lamellae, etc.) could be produced unstably but persistently in alloys under non-equilibrium conditions. It is significant that during Fe-Mo diffusion, the transient N phase occurred only at 1,400°C (temperature within the σ -range where it impedes ξ) and at 800°C (where it precedes ξ in sluggish reaction), but not at 1,100°C, where reaction towards ξ can proceed rapidly and without impediment. The N formation at 800°C further implies the interesting fact that in Fe-Mo a σ -type phase can form unstably already at the same low temperature at which it does stably in Fe-Cr.

The concepts of the 'latent', 'transient', and 'pseudo'-miscibility bays of which these are instances, again link with the picture of unity in transition metal alloy systems, developed in the first section. Intermetallic compound formation as discussed below, provides a further variation upon this theme.

THE ROLE OF LAVES AND SIGMA TYPE PHASES

Laves phases

The structural knowledge of the Laves type phases is extensive, and reference to the literature must suffice¹². Several points should, however, be brought out in relation to Nb-base alloys. The three subgroups (cubic MgCu_2 , hexagonal MgZn_2 and MgNi_2 types) are of layer structures involving stacking differences similar to those known in the pure metals. Taking NbCr_2 , NbFe_2 and ZrFe_2 * as examples for each of the three types, we have¹³ hexagonal double layers of the larger Nb (Zr) atoms, with a tetrahedral environment of Cr (Fe), but differing thus:

	<i>Stacking sequence</i>
In NbCr_2 and elemental cubic close-packing (FCC)	ABCABC . . .
In NbFe_2 and elemental hexagonal close-packing (HCP)	ABABAB . . .
In ZrFe_2 — hybrid of both (not known in elements but in Ni_3Ti)	ABACABAC . . .

Furthermore, geometrically the Laves phase structures are unique in being those of the most economic occupation of space by two types of spheres. The condition of atomic diameter ratio $-\sqrt{3/2} = 1.225$ (ideally), applies, within 8%, to the observed

* High temperature form. The MgNi_2 class is rare, and Nb-bearing representatives do not seem to have been found; see Fig. 6.

transition metal compounds. Fundamentally, therefore, whilst the elemental structures and their solid solutions are closest-packing only within the constraint of prescribed diameters, the Laves phases are closest-packing for optimum diameters. Therefore, not only will Laves phase formation from a Nb-base matrix be associated with considerable contraction (a feature, incidentally, which has a major bearing on alloy properties, including oxidation resistance); it also represents a continuation of the tendency towards densest packing, expressed within the transition metal block of the periodic table by the adoption, for the *higher* atomic numbers of each period, of FCC and HCP structures, for the *lower* ones, of the Laves structures and, in certain intermediate cases, of the σ -structures.

Although Laves phases are essentially size-factor compounds, electron concentration is still important, particularly in deciding the stacking type to occur, and the co-existence of certain Laves phases where size-factor would have been favourable¹³.

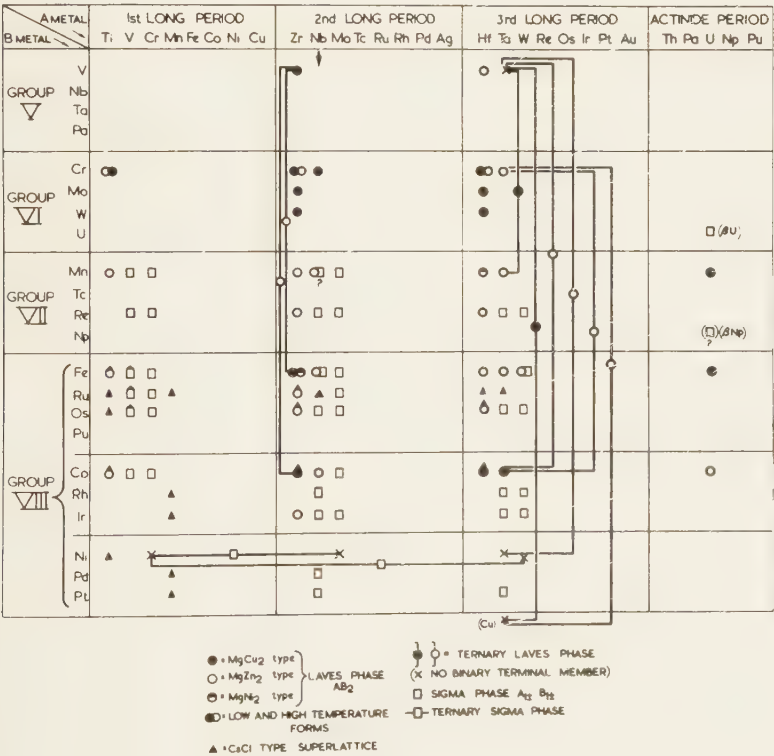


Fig. 6. Binary and ternary Laves, sigma and CsCl type phases amongst transition metals surrounding niobium.

In Fig. 6 the occurrence of transition metal Laves and sigma phases has been systematised (from various sources), showing the place of Nb within this wider framework. The few ternary compounds so far known are also indicated. Of the many implications, we should briefly point to: (1) The *systematic run* of the 3 stacking types, such as the transition along each period, from cubic to hexagonal and back again, which can

be related to electron/atom ratio; the change-over for $\text{NbCr}_2 \leftrightarrow \text{NbMn}_2$ and $\text{NbCr}_2 \leftrightarrow \text{TaCr}_2$ is noted. (2) The *allotropic transformations* within individual, critically placed, Laves phases: a remarkable feature here is the inversion between TiCr_2 and ZrCr_2 , of the hexagonal $\leftrightarrow$ cubic sequences with temperature. (3) The occurrence of pure *ternary* Laves phases, where binary terminal members may not exist (*e.g.* cubic $\text{TaV}_{1.5}\text{Mn}_{0.5}$, hexagonal $\text{TaV}_{1.5}\text{Cu}_{0.5}$); also in a ternary system such as Zr-V-Co , the section $\text{ZrV}_2\text{-ZrCo}_2$ contains cubic terminal, but hexagonal intermediate phases. Niobium-bearing analogues, though not yet reported, will almost certainly occur (which would affect the $\text{L}_1\text{-L}_3$ sections in Fig. 2). In terms of free energy, the position can again be summarized by assuming for the cubic and hexagonal Laves phases near-parallel curves of only slightly different radius, intersecting at obtuse angles as a function of temperature and of composition within the periodic table.

In the present work, a ternary *silicon*-bearing Laves phase $\text{Cr}_5\text{Nb}_3\text{Si}_2$ was observed (see next section); electron supply by Si addition transforms the cubic NbCr_2 to the hexagonal NbFe_2 type. Correspondingly in the Nb-Fe-Si system¹⁴, NbFe_2 dissolves Si to extensive amounts.

One important feature of the Laves phases, which often seems neglected, is their deviation from stoichiometry AB_2 . Considerable binary homogeneity ranges around NbFe_2 and CrNb_2 have been found, and it may be said that, whilst in the primary BCC metals, the replacement of Fe or Cr by Nb is very restricted, transformation to Laves structure is a means of enhancing it.

Sigma phases

The pattern of *sigma* phase occurrence¹⁵ (also Fig. 6) shows a close correlation with that of the Laves phases. *Nb*-base σ -phases appear mostly in combination with the heavier Group VII and VIII metals, but the existence of σ Nb-Fe ¹⁴ (and possibly Nb-Mn) is known.

The σ -phases present a further mode of realisation of close-packing, alternative to the FCC, HCP and Laves modes, and pertain to intermediate atomic size and electron/atom ratios. The σ -structure (for full description see ref. 16) again contains pseudo-hexagonal layers, but puckered in characteristic fashion. There exists a most interesting and readily derived structural relationship between (a) the Laves phases, (b) σ , and (c) the BCC as common parent, and considered as layer-lattices, this provides a helpful approach in explaining the mechanism of mutual transformation. It may be noted that the σ -phases are preferred in those systems which also favour extensive BCC matrix solutions, the Laves phases in those where the latter are restricted; both can coexist only in a few borderline cases. Both the σ and Laves phases are basically capable of forming without diffusion from BCC (*e.g.* in FeCr and TiCr_2), though only at singular compositions; in *Nb*-base systems, *e.g.* Nb-Cr-Mo , diffusion is generally involved.

To set against the above silicon-bearing ternary Laves phases, the parallel case of stabilisation of σ -phases by Si is of course well established, *e.g.* in Fe-Cr-Si , Ni-Cr-Si , Fe-V-Si , etc.¹⁷.

Other intermediate phases and comment

The potential formation of CsCl type *superlattices* in the BCC structure is here

important and may well precede σ or Laves phase formation in Nb-systems. CsCl type phases, also marked in Fig. 6, have been reported in many of the present transition metal systems¹⁸ at mid-composition, such as TiFe. The known existence of VRu and LaRu superlattices made a similar "NbRu" likely, which was confirmed by DWIGHT; generally, a degree of ordering in Nb-base alloys should occur under Group VIII combinations, either preparatory to compound precipitation or stably within the matrix*; however, this may often remain latent or unobserved owing to unfavourable X-ray absorption conditions.

The " β -W", α -Mn (χ -phase), β -Mn, VCo₃, TiCu₃ and other types of intermediate compounds can only be noted, except for a comment below on β -W, but their correlations follow lines similar to those in Fig. 6.

In principle, all these phases represent demonstrable variants to the above themes of: (1) structural derivatives from the BCC and (2) layer lattices in different stages of close-packing. Strikingly this includes also actual HCP (quasi-elemental) intermediate phases.

In niobium alloy development, σ , Laves and associated phase nucleation may be considered beneficial, whilst incipient, in promoting mechanical strength; their fuller precipitation is embrittling, but can be avoided or controlled by composition and heat-treatment choice, for instance again employing our miscibility bay reasoning and the basic arguments of the previous sections.

It is of some interest that the W₃O (" β -W") type lattice occurs in Nb systems for Nb₃Rh, Nb₃Os, Nb₃Ir, Nb₃Pt and Nb₃Au, being associated (Fig. 6) with σ -formation, but also for Nb₃Sn and Nb₃Sb. This implies not only that its stabilisation is likely on noble metal, tin or antimony addition, but that, in the presence of oxygen, a suboxide Nb₃W₃O (non-existent in the binary Nb-O system) could be promoted by tungsten with further ternary combinations, and play an important part in oxidation behaviour.

COMPOUND-DOMINATED TERNARIES

The numerous binary compounds of niobium with non-transition metals can only be referred to here².

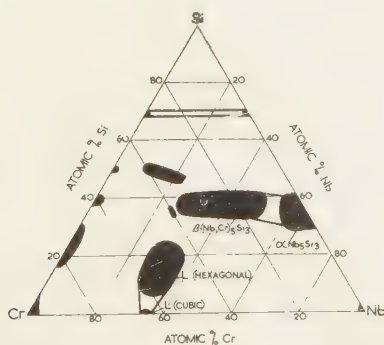


Fig. 7. Cr-Nb-Si diagram (single phase fields); 1,000°C section.

It is suggested that some of the reported CsCl structures in Fig. 6 may cover a (not yet observed) sluggish phase-change at low temperatures.

The sparse data available on Nb-bearing ternary systems deal largely with pseudo-binary sections between phases. Table II summarizes such data involving Si, B, C and N, with some annotations.

TABLE II
NIOBIUM-BASED TERNARY SYSTEMS WITH Si, B, C AND N*
(Survey of available work)

System	Data	Reference
Nb-V-Si	V ₃ Si (Al ₁₅ type) dissolves to 32 mole % Nb ₍₃₎ Si. <i>Nb₅Si₃-V₅Si₃</i> section: solution in α and β forms extensive; coexist with (Nb,V) metal.	24
Nb-Me-Si	<i>NbSi₂-VSi₂</i> section: CSS** (C ₄₀ type). [Partial or complete solutions probable also between: Nb ₄ Si-Ta ₄ Si; Nb ₅ Si ₃ -(Ta, V, Ti, Zr, Hf, Mo, W) ₅ Si ₃ ; NbSi ₂ -(Ti, Zr, Hf, V, Ta, W)Si ₂ .]	25
Nb-Cr-Si	See Text	
Nb-Fe-Si	See Text	
Nb-Ti-B	<i>NbB₂-TiB₂-ZrB₂-CrB₂</i> : CSS (C ₃₂ , AlB ₂ type).	26
Nb-Zr-B	[Probably also CSS with HfB ₂ , VB ₂ , TaB ₂ , MoB ₂ . AlB ₂ isomorphism suggests extensive Al replaceability; Nb-Al-(B,Si) systems merit special attention.]	
Nb-Cr-B		
Nb-Me-B (Effect of Al)		
Nb-Me-(Si,B) (Effect of Ge)	[Isomorphism α Nb ₅ Si ₃ -Cr ₅ B ₃ and structural factors suggest extensive silicide-boride substitutions. Note: (Nb,V,Ta,Cr)Si ₂ and (Nb,Ta)Ge ₂ isotypes. Effect of germanium merits attention.]	
Nb-Cr-C	η_1 type carbide Nb ₃ Cr ₃ C	
Nb-(V,Ni)-C	η_1 " " Nb ₃ (V,Ni) ₃ C	27
Nb-(Ti,Ni)-C	η_2 " " (Nb,Ti) ₄ Ni ₂ C [Alloy steel carbides Me ₂₃ C ₆ , Me ₇ C ₃ also dissolve minor Nb, Me ₆ C (η) more; but NbC very stable.]	
NbC-MeC-MeN	<i>NbC-TiC, -ZrC, -HfC, -VC, -TaC, -UC; -NbN, -VN</i> : CSS (FCC) <i>NbC-Mo₂C</i> : to > 60 mole % Mo ₂ C. (<i>Nb,Ta</i>)C-WC: to 40 mole % WC at 2,100°C, decreasing with temperature. [Defect lattices to (Nb,Me) ₄ C ₃ ; stacking fault liability (transition to Me ₂ X below).]	28, 29
Nb ₂ C-Me ₂ C-Me ₂ N	Partial or complete solubility (HCP): <i>Nb₂C-V₂C, -Ta₂C, -Mo₂C, -W₂C</i> ; <i>Nb₂C-V₂N, -Ta₂N, -Cr₂N, -Mo₂N, -W₂N, -Mn₂N</i> , possibly $-\epsilon$ (Fe base) carbide/nitride (some metastable).	30
NbN-MeC-MeN	<i>NbN-TiC, VC, TiN, VN, ZrN</i> : CSS. [No doubt also CSS with some other Group IV, V, VI mono-carbide/nitride isomorphs.]	28, 29
Nb-C-N	NbC-NbN and Nb ₂ C-Nb ₂ N: CSS.	29, 30
Nb-Si-C } Nb-Si-N }	Ternary compounds Nb _x (Si,C) and Nb _x (Si,N) occur of D _{8g} type, adjoining Nb ₅ Si ₃ . (Nowotny phases)	24, 31
Nb-Si-B	Appreciable primary solubility of B in Nb silicides. Compound Nb _x (Si,B) occurs, also D _{8g} type.	24

* For reference, the basic binary compounds are: Nb₄Si; α, β Nb₅Si₃; NbSi₂. Nb₃B₂; NbB; Nb₃B₄; NbB₂. Nb₂C; NbC; Nb₂N; NbN (with C,N deficiencies).

** CSS = Complete solid solubility.

[] = Author's remark.

The Fe-Nb-Si and Cr-Nb-Si systems recently investigated (1,000°C sections) represent, it is believed, some of the first niobium-bearing overall diagrams. The former has already been described¹⁴. A full account on the Cr-Nb-Si diagram will be given elsewhere, but an outline is shown in Fig. 7 (single phase fields only, except between related structure pairs). The essential points here are: (1) the complexity of equilibria, involving 5 new ternary and 11 binary phases; (2) the stabilisation of the ternary Laves phase by Si; (3) that of the high temperature (β) form of Nb₅Si₃ by Cr, to give a genuine ternary compound along the (Nb, Cr)₅Si₃ section; (4) along CrSi₂ $\leftrightarrow$ NbSi₂, the mutual insolubility despite isomorphy, due to unfavourable size-factor, and contrasting with more normal disilicide solubilities (in VSi₂-NbSi₂ etc.); and (5) the wide homogeneity ranges of three of the ternary silicides, accompanied by lattice spacing changes.

Alloys in systems such as these are generally limited in application through their brittleness; however, the compounds are of interest from the oxidation resistance aspect, and when bonded with ductile matrices (*e.g.* in metal ceramics), also in their role as possible precipitation hardening agents in niobium-base alloys. Attention is drawn to the structural influence (Table II) of boron, aluminium and germanium in conjunction with silicon, and its possible practical interest.

(The related ternary silicides, recently reported by WESTBROOK¹⁹ in Ti-Ni-Si should be mentioned, similarly BEATTIE's "G" phase²⁰, and other steel-extracted compounds in which Si and Group IV to VI metals are integral.)

Concerning the Nb-bearing *carbide* and *nitride* systems of Table II the feature of non-stoichiometry (C deficiency) in NbC and Nb₂C is important, being variable and controllable by ternary additions. Furthermore, we may formulate the following practical rule, well founded on size factor:

The close-packed (Nb, Me) (C, N) and (Nb, Me)₂(C, N) type compounds are favoured by those (Nb, Me) couples, which *without* C or N, are mutually soluble; whereas those (Nb, Me) couples which, *without* (C, N) favour Laves (partially σ) phases and restricted primary solutions, form *with* (C, N) the ternary *eta* carbide (Me₆X) types. The latter is readily verified by comparing Fig. 6 with the known eta-carbide isomorphs. A closer study of the crystal structure of Laves and eta phases well explains the transformation mechanism imposed by attempted carbon insertion in the 'ideal' close-packed lattice.

The fact of NbC-Nb₂C occurrence being linked, upon carbon abstraction, with the BCC solid solutions, is further reflected in the ternary systems NbX-AX-BX (X = interstitial) and Nb-A-B, particularly in their ability to form quite analogous miscibility bays. For example, in NbC-ZrC-VC²¹ a bay occurs, congruent to that in Nb-Zr-V (Fig. 2). Furthermore, much of the above discussion regarding stacking order in pure metal Nb-base alloy systems, applies to the corresponding cubic and hexagonal interstitial compound ternary systems.

The ternary Nb silicides would lead on to ternary *aluminides*, similarly of interest for oxidation resistance; however, apart from the compound NbAl₃ (AuCu₃ structure), there seems little known even on the Nb-Al binary*. Size-factor (only 2.7% difference) favours large primary Nb-Al solubility, but electron concentration militates

* Very recently a phase Nb₂Al of sigma structure²² and one of Nb₃Al of beta-W structure²³ have been reported. If confirmed this would be of unusual theoretical interest.

against it. No ternary work whatever seems to be available, and study of systems such as Nb-Si-Al, Nb-Ni-Al, Nb-Ti-Al and their quaternary combinations would be much worthwhile, both from the constitutional and properties aspects. TiAl_3 , ZrAl_3 and NbAl_3 are isotypic, and probably intersoluble.

The interstitial alloys above would lead naturally to the ternary niobium oxide systems Nb-Me-O; however, an account of this subject, on which the author has carried out a major separate investigation, will be given elsewhere.

CONCLUSION

In review, constitutional work on niobium-base ternary (and higher) alloy systems can well assist in giving a lead to develop high temperature strength and (in conjunction with Nb-Me-O systems), oxidation resistance. In particular, the evolution of miscibility bays in transition metal solid solution diagrams, and the associated effects (incipient precipitation both of BCC isomorphs and of compounds such as Laves and σ -phases) give a means to induce age-hardening effects by sensitive composition and heat-treatment control. The Nb-Cr-Mo system investigated illustrates this.

Transitory (non-equilibrium) conditions during diffusion can, in the Group IV to VIII systems surrounding niobium, assume the role of "quasi-equilibria" and introduce distinctive constitutional stages and behaviours, of some fundamental, and, if caused to persist, probable practical interest. Further basic implications within this scheme attach to the character of Laves and other inter-transition metal phases which have been discussed, their evolution from the matrix structure through atomic re-layering and ordering.

Amongst the compound-dominated niobium systems, the Nb-Cr-Si system studied involves new ternary compounds, a hexagonal Laves phase amongst them. A review also of ternary Nb carbide, nitride, boride and associated systems indicates conspicuous gaps in available knowledge and approaches to further work.

As unifying theme to all these reactions, the viewpoint is put forward of *submergence*, in transition metal alloys, of the pure elements and the elevation to near-elemental equivalence of each of their mutual alloy states; niobium is considered in this sense as but a near-equal partner with its alloys.

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THE PHYSICAL PROPERTIES OF NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN

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SUMMARY

The physical properties of niobium, tantalum, molybdenum and tungsten are reviewed in relation to the properties of the other elements of groups IVa, Va and VIa of the periodic table. Zone-refined specimens of niobium and tantalum have been prepared and resistivity, magnetic susceptibility and thermal e.m.f. measurements made in the temperature range 10°–295°K.

INTRODUCTION

The electronic structure of the free atoms of the elements of groups IVa, Va, and VIa are given in Table I.

The elements of the second transition group have structures which suggest that the $4d$ levels are relatively lower compared with the $5s$ levels than the analogous $3d$ and $4s$ or $5d$ and $6s$ levels of the first and third long periods. Chromium and molybdenum have a half-filled d shell and 1 electron in the $4s$ or $5s$ level; this effect is not continued by tungsten, which has a $5d^46s^2$ ground state.

Recently¹ attempts have been made to discuss the crystal structure of the transition metals in terms of a localised wave function approach and these considerations have led to the suggestion that the body-centred-cubic structure of the elements of groups Va and VIa may be associated with a high percentage of 'd character' in the

TABLE I
THE ELECTRONIC STRUCTURE OF THE FREE ATOMS OF THE ELEMENTS OF GROUPS IVa, Va AND VIa

Element	K		L			M			N				O				P
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s		
Ti	2	2	6	2	6	2	2										
V	2	2	6	2	6	3	2										
Cr	2	2	6	2	6	5	1										
Zr	2	2	6	2	6	10	2	6	2	—	2						
Nb	2	2	6	2	6	10	2	6	4	—	1						
Mo	2	2	6	2	6	10	2	6	5	—	1						
Hf	2	2	6	2	6	10	2	6	10	14	2	6	2	—			2
Ta	2	2	6	2	6	10	2	6	10	14	2	6	3	—			2
W	2	2	6	2	6	10	2	6	10	14	2	6	4	—			2

bond hybrids. The electronic structure of the solid transition metals is not, however, understood in any detail. MOTT AND STEVENS² and LOMER AND MARSHALL³ discussed the elements of the first long period using data obtained by WEISS AND DEMARCO⁴, but this work is strongly contested by several authorities on both experimental and theoretical grounds.

Band structure calculations⁵ for iron suggest a maximum in the density of states curve at 5.6 electrons/atom and another maximum at higher electron concentrations; the values of the electronic specific heat and the susceptibilities of the elements of the first long period tend to support this suggestion⁶. Very few calculations of band structure have been made for the second and third long periods, and CALLAWAY⁷ suggests that these pre-war cellular calculations should be disregarded since the workers in general paid insufficient attention to the boundary conditions. Thus the only satisfactory guide to the electronic structure of these elements is the electronic specific heat and the susceptibility. These properties suggest a sequence of structures rather similar to that found in the first transition series.

Tables II, III and IV contain a summary of the physical properties of the elements of groups IVa, Va, VIa. Certain properties such as the electronic specific heats and the susceptibilities show a pronounced maximum at group Va and these effects may be compared with those occurring at group VIIc. It is possible that the density of states curves show two peaks for elements of all the three periods and that this is reflected in these properties. However, other properties such as the interatomic distances, the compressibilities, the coefficients of expansion, heats of sublimation and melting points all suggest that the maximum strength of bonding is reached in the elements of group VIa and that the strength of bonding in each group increases on passing from the 1st $\rightarrow$ 2nd $\rightarrow$ 3rd long period⁶.

WHITE AND WOODS⁸ have compared the ideal electrical (ϱ_i) the thermal (W_i) resistivities (due to scattering of electrons by thermal vibrations), deduced from low temperature measurements of thermal and electrical resistivity, with the predictions of standard theory⁹. The ideal electrical resistivity of the transition elements of groups IVa, Va and VIa followed a Bloch-Grüneisen function down to $\theta_D/5$, where θ_D is the Debye temperature.

$$\text{i.e.} \quad \varrho_i = 4 \pi A (T/\theta)^5 J_5 \quad (1)$$

$$\text{where} \quad J_n(\theta/T) = \int_0^{\theta/T} \frac{x^n dx}{(e^x - 1)(1 - e^{-x})}$$

$$\text{For} \quad \begin{array}{ll} T \ll \theta & \varrho_i \propto T^5 \\ T > \theta & \varrho_i \propto T \end{array}$$

In general, the ideal thermal resistivity could be approximated by the relation

$$W_i/W_\infty = 2(T/\theta)^2 J_3(\theta/T) \quad (2)$$

where W_∞ is the ideal thermal resistivity at high temperatures. For $T/\theta_D = 0.2$ eqn. (1) gives $\varrho_i/\varrho_\theta = 0.068$, where ϱ_θ is the ideal electrical resistivity at $T = \theta$ and from Table II it can be seen that this is approximately true.

TABLE II
PHYSICAL PROPERTIES OF THE ELEMENTS OF GROUPS IVa, Va AND VIa

Property	Element	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
Atomic no.		22	40	72	23	41	73	24	42	74
Atomic wt.		47.9	91.2	178.6	50.9	92.9	180.9	52.0	95.9	183.9
Closest distance of approach kX		$\alpha 2.92$ $\beta 2.87$	$\alpha 3.17$ $\beta 3.13$	3.14	2.63	2.85	2.85	2.49	2.72	2.74
Compressibility ($\text{kg}^{-1} \text{cm}^2 \times 10^6$ at 10,000 kg/cm^2)		1.09	1.02	0.90	0.59	0.57	0.48	0.55	0.55	0.29
Melting point ($^{\circ}\text{C}$)		1,660	1,860	2,225	1,860	2,468	2,980	1,850	2,600	3,380
Coefficient of thermal expansion $^{\circ}\text{C}^{-1} \times 10^6$ (0–100 $^{\circ}\text{C}$)		8.4	5.9	6.0	8.3	7.0	6.6	5.9	5.2	4.5
Thermal conductivity ($\text{W}/\text{cm}^{\circ}\text{C}$)		0.20	0.21	0.22	0.36	0.53	0.54	0.86	1.45	1.7
Latent heat of fusion (kcal/mole)		4.5	4.6	—	—	—	5.9	4.6	6.6	8.4
Latent heat of sublimation at melting point (kcal/mole)		106.2	137.9	—	119.9	—	183.9	90.4	134.5	—
Debye θ										
low temperature		430	310	261	273	252	231	630	445	380
high temperature		360	250	210	390	250	230	480	380	315
γ (10^{-3} J/mole.deg ^{2})		3.3	3.0	2.6	9.0	9.2	5.9	1.5	2.1	1.2
Susceptibility (e.m.u. $\times 10^6/\text{g atom}$)										
20 $^{\circ}\text{C}$		153	119	75	255	204	149	190	87	59
high temperature		202 (777)	173 (900)	— (900)	233 (1,700)	166 (1,575)	121 (1,850)	218 (1,400)	104 (1,825)	68 (1,850)
Resistivity ($\mu\Omega \cdot \text{cm}$)		43.1	42.4	30.6	19.9	14.5	13.1	12.9	5.3	5.3
Temperature coefficient of resistivity ($\times 10^3/^{\circ}\text{C}$)		4.10	4.35	(6.2)	3.40	3.95	3.82	2.14	4.23	4.80
$\rho_{0.2\theta}/\rho_{\theta}$		0.068	0.065	0.067	0.093	0.079	0.076	0.072	0.061	0.054

Vanadium shows the greatest deviation and this can possibly be attributed to electron-electron interactions, which are likely to be important in this element since the electronic specific heat and susceptibility both suggest a high density of states at the Fermi surface. Although θ_i may adequately be represented over a fairly wide temperature range by a suitable choice of θ , no single value gives good agreement from high to low temperatures. Values of θ_D calculated from specific heat measurements made in the temperature range $\theta/2$ to θ and also at low temperatures $\sim 10^\circ\text{K}$ are included in Table II. Variations in θ_D of $\sim 100^\circ\text{K}$ are apparently quite common.

Tables III and IV give the equations developed by KUBASCHEWSKI AND EVANS¹⁰ or KELLEY¹¹ for the high temperature specific heat and vapour pressure of the elements of groups IVa, Va, VIa. The fact that the specific heats of these elements do not approach the value suggested by Dulong and Petit's law ($C_P = 6 \text{ cal/deg.g atom}$) is an indication of the comparatively large influence of the electronic specific heat in these elements since the difference between C_P and C_V is only $\sim 0.2\text{--}0.5 \text{ cal/deg.g atom}$. On the other hand there is no immediate explanation of the large variations in the vapour pressures of these elements at their melting points (from $3.9 \cdot 10^{-3} \text{ Hg}$ for chromium to $1.3 \cdot 10^{-2} \text{ Hg}$ for zirconium) and this emphasizes the very limited understanding that we have of the properties of these elements.

TABLE III

MOLAR SPECIFIC HEAT (C_P) FOR THE ELEMENTS OF GROUPS IVa, Va AND VIa^{10,11}

Element	$C_P = a + bT + cT^{-2} \text{ (cal/}^\circ\text{C.mole)}$		
	a	$b \cdot 10^3$	$c \cdot 10^{-6}$
Ti	5.28	2.4	—
	6.91	—	—
Zr	6.83	1.12	—0.91
	7.27	—	—
Hf	—	—	—
V	5.40	2.00	—
Nb	5.66	0.96	—
Ta	5.82	0.78	—
Cr	5.84	2.36	—0.88
Mo	5.48	1.30	—
W	5.74	0.76	—

TABLE IV

VAPOUR PRESSURES OF THE SOLID ELEMENTS OF GROUPS IVa, Va AND VIa¹⁰

Element	$\log_{10} p = AT^{-1} + B \log_{10} T + CT + D \text{ (mm Hg)}$				
	A	B	$C \cdot 10^3$	D	$p \text{ at m.pt.}$
Ti	—24,275	—	—0.23	10.66	$4.8 \cdot 10^{-3}$
Zr	—31,070	—	—0.2415	10.215	$1.3 \cdot 10^{-5}$
Hf	—	—	—	—	—
V	—26,650	—	—0.112	10.815	$1.17 \cdot 10^{-2}$
Nb	—	—	—	—	—
Ta	—41,600	—1.0	—	13.98	$4.5 \cdot 10^{-3}$
Cr	—21,200	—1.56	—	15.75	3.9
Mo	—31,060	—0.2	—	9.41	$7.9 \cdot 10^{-3}$
W	—42,00	+0.146	—0.164	9.84	$1.78 \cdot 10^{-2}$

PROPERTIES OF ZONE-REFINED NIOBIUM AND TANTALUM

Niobium supplied by Murex Ltd. and tantalum supplied by Ciba Ltd. (analyses in Table V) have been zone-refined by an electron bombardment floating zone technique which follows the general lines described by CALVERLEY, LEVER AND DAVIS¹². In the present work the filament was traversed from the bottom to the top of the specimen. The zone-refining unit was contained in a chamber which could be evacuated by a 9 in. oil diffusion pump to a pressure of $1.6 \cdot 10^{-6}$ mm Hg. In normal operation the unit had an apparent leak rate of 0.3 lusec.

TABLE V
ANALYSES OF NIOBIUM AND TANTALUM BEFORE ZONE REFINING

Impurity	Material	
	Niobium	Tantalum
C	0.01%	0.05%
O ₂	0.007%	0.02%
Ta	<0.3%	
Nb		<0.01%
W	trace	<0.01%
Mo	not detected	<0.01%
Sn	not detected	<0.01%
Fe	<0.07%	0.02%
Ni		0.02%

Rods of niobium and tantalum approximately 12.5 cm long and 0.55 cm diameter were given one pass at 10 cm/h and 6 slow passes at 4.3 cm/h. They were then swaged to 0.25 cm diameter and the best section selected by resistivity measurements. Fig. 1 shows the variation in resistivity along a zone-refined rod of niobium. The best section was cut from the rod and divided into two parts; one was annealed for one hour at 1,200°C in a vacuum of $< 10^{-5}$ mm Hg and a single crystal was grown from the other by a zone-melting technique. A niobium filament was used for the niobium specimens and a tantalum filament for the tantalum specimens during zone refining and crystal growth.

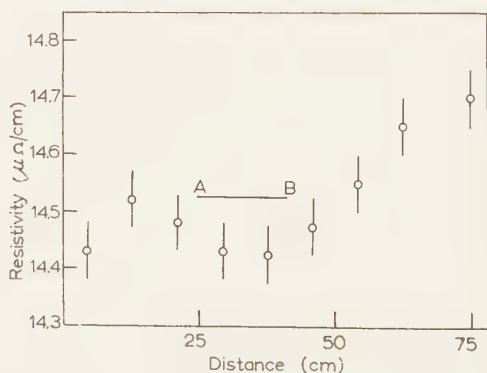


Fig. 1. Resistivities measured along the length of a zone-refined niobium rod. The zone was traversed in the direction AB.

RESISTIVITY

Resistivities were determined using a standard resistance and a simple potentiometric technique.

The resistivity/temperature curves are shown in Figs. 2 and 3 and it would appear that an appreciable resistivity is associated with the presence of grain boundaries. However, the geometry of the single crystal specimens was not sufficiently well controlled to warrant more detailed discussion of this factor. The ratio of the resistance at room temperature to that at 10°K is greater for the tantalum single crystal (249) than for the niobium specimen (48). Zoning at one half the speed increased the ratio

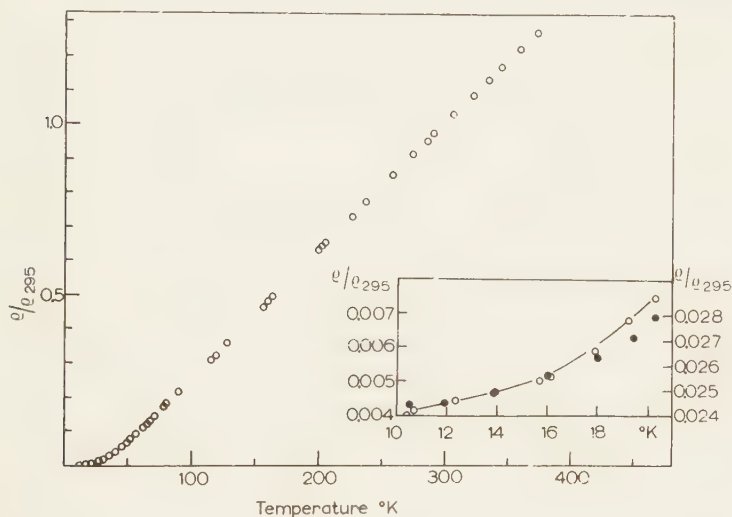


Fig. 2. Resistivity of zone-refined tantalum. $\circ$ = single crystal (L.H. scale). $\bullet$ = polycrystal (R.H. scale). $\rho_{295} = 13.8 \mu\Omega\text{cm}$ zoned at 4.3 cm/h.

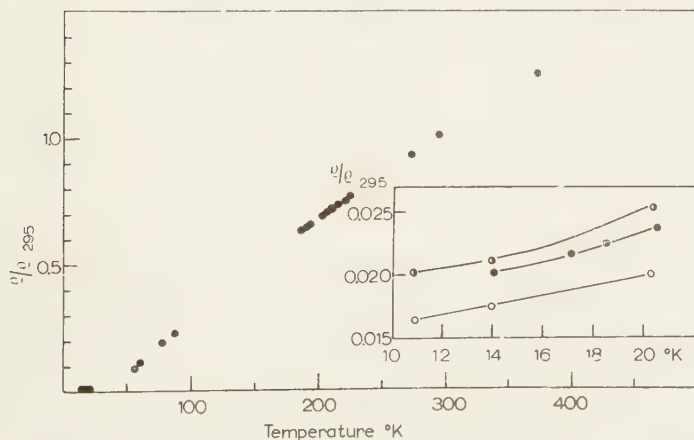


Fig. 3. Resistivity of zone-refined niobium. $\circ$ = single crystal. $\bullet$ = polycrystal. $\rho_{295} = 14.5 \mu\Omega\text{cm}$ zoned at 2.1 cm/h. $\odot$ = single crystal zoned at 4.3 cm/h.

for the niobium to 6r. These results may be compared with those quoted by CALVERT¹³ (tantalum 72, niobium 205). Since the techniques used and the precautions taken in his work are rather similar to those of the present work, the differences are probably due to differences in the starting materials. It is possible to purify molybdenum, tungsten, niobium and tantalum by volatilising such elements as iron and chromium and the suboxides of the refractory metals. Other elements such as carbon can be efficiently zoned, but the removal of the more refractory elements by zone

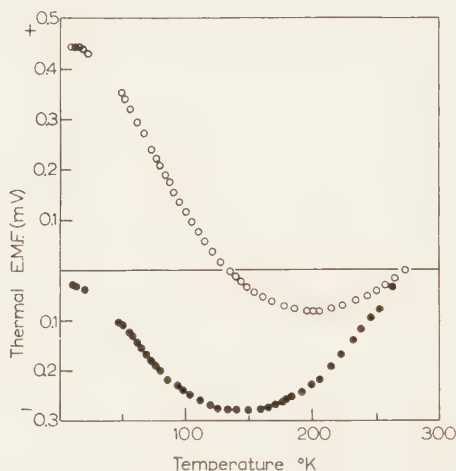


Fig. 4. Thermal e.m.f. of zone-refined tantalum. O (zoned at 4.3 cm/h), and of zone-refined niobium. ● (zoned at 2.1 cm/h) relative to platinum (Pt-ve).

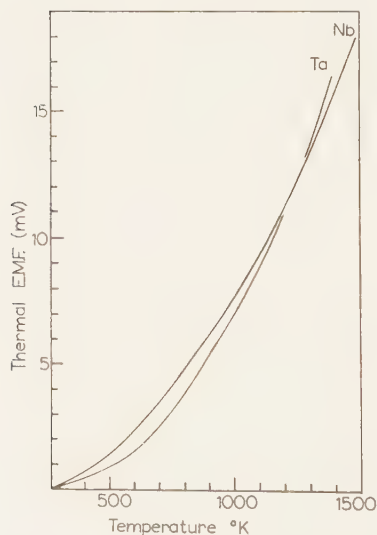


Fig. 5. Thermal e.m.f. of zone-refined tantalum and niobium relative to platinum (Pt-ve).

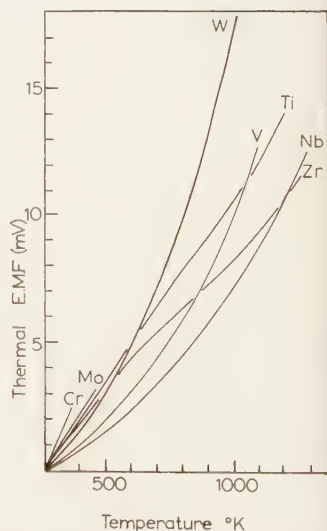


Fig. 6. Thermal e.m.f. of elements of groups IVa, Va and VIa relative to platinum (Pt-ve).

refining appears to be very slow. This is perhaps not surprising since the difference in the slopes of the liquidus and solidus curves are not likely to be great and therefore the distribution coefficient for these elements will be near to 1.

THERMAL E.M.F.

The thermal e.m.f.'s of zone-refined niobium and tantalum as measured against Johnson Matthey 'Thermopure' platinum are shown in Figs. 4 and 5. High temperature measurements were made in a vacuum of $< 10^{-5}$ mm Hg. At low temperatures the thermal e.m.f. of the niobium/platinum couple approaches zero but the tantalum/platinum couple tends to a limit at 0.45 mV (platinum negative). At high temperatures the output of the tantalum/platinum couple is slightly higher than the niobium/platinum couple and Fig. 6 compares these thermocouples with other refractory metal couples. The relative e.m.f.'s of the thermocouples vary with temperature but at high temperatures the elements of group VIa probably give the greatest e.m.f. and the elements of group IVa the least.

MAGNETIC SUSCEPTIBILITY

Table VI shows the magnetic susceptibility of zone-refined niobium and tantalum at three temperatures. No systematic variation with field was found in the range 0-11 kOe and the values quoted are mean values for this range of fields. All measurements were made using a Sucksmith ring balance calibrated with pure platinum. The accuracy of the measurements is not very high since the masses used were only of the order of 100 mg. However, the absolute values are in agreement with previous work.

TABLE VI

THE MAGNETIC SUSCEPTIBILITY (e.m.u./g) OF ZONE-REFINED NIOBIUM AND TANTALUM

Temperature °K	Element	
	Nb	Ta
294	$2.4 \pm 0.06 \cdot 10^{-6}$	$0.9 \pm 0.06 \cdot 10^{-6}$
78	$2.4 \pm 0.06 \cdot 10^{-6}$	$0.9 \pm 0.06 \cdot 10^{-6}$
20	$2.5 \pm 0.06 \cdot 10^{-6}$	$1.0 \pm 0.06 \cdot 10^{-6}$

CONCLUSIONS

Most of the physical properties of the transition elements suggest that there is a maximum in the bonding strength at either group Va or VIa, but the understanding of the transition elements is not yet at a stage where this can be adequately explained. Recent work on zone-refined niobium and tantalum has shown considerably lower residual resistivity values than had previously been reported and it is to be expected that other properties which are sensitive to small amounts of impurity will be subject to correction.

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THE ANNEALING OF WORKED TUNGSTEN

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SUMMARY

Structural changes occurring during the annealing of worked tungsten have been followed using the transmission electron microscopy technique. It is suggested that the technique could be used as a means of studying the effect of additions on the recrystallisation process.

The observations are related to the brittleness of tungsten.

INTRODUCTION

Control of recrystallisation is very important in the fabrication of tungsten¹. The recrystallisation can be controlled by the addition of various oxides, but although this

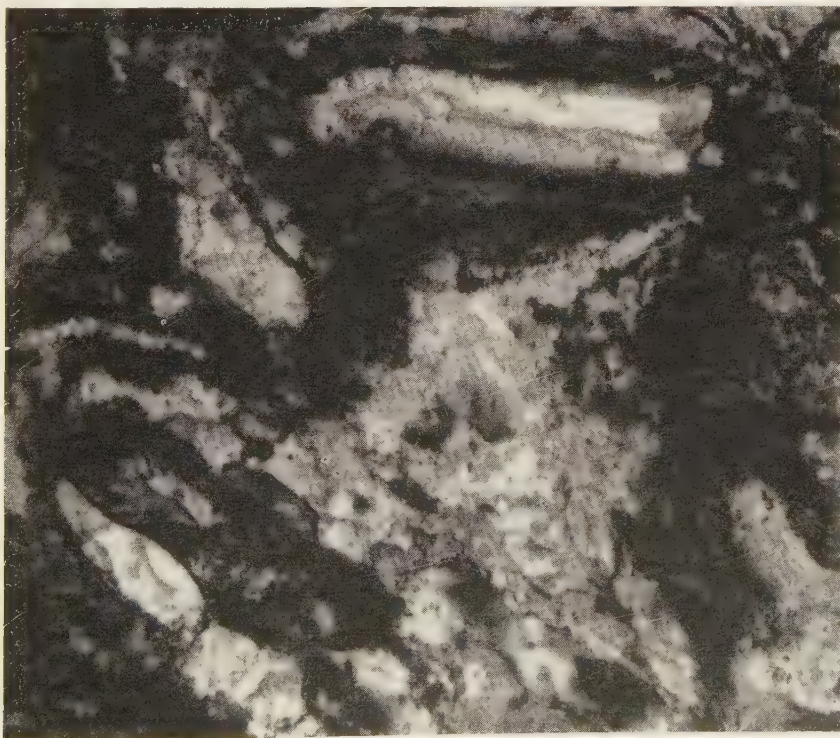


Fig. 1. As-received tungsten. ($\times 36,000$)

technique is widely used it is not fully understood. In the series of experiments described in the present paper, the recrystallisation of tungsten has been examined using transmission electron microscopy. The commencement of recrystallisation has been observed and from the observations it seems that transmission electron microscopy can be a very powerful tool for the examination of the effect of additions on recrystallisation. The relevance of the observations to the brittleness of tungsten is also considered.

MATERIAL USED

The tungsten used was in the form of ribbon $25\ \mu$ thick $\times$ 1.5 mm wide, supplied by Metallwerk Plansee, Reutte, and was presumed to be in a heavily worked condition (see the Section dealing with the experimental observations).

EXPERIMENTAL TECHNIQUES

Each specimen was prepared by electropolishing the tungsten ribbon between parallel stainless steel sheet cathodes in a 2% sodium hydroxide solution, using a supply of about 9 V unsmoothed rectified a.c. Before electropolishing, the specimen edges and that region of the specimen near the air/electrolyte interface was masked off with "Lacomit" lacquer. The electropolishing was continued until two holes had almost met, when the specimen was thoroughly washed with water and then alcohol before

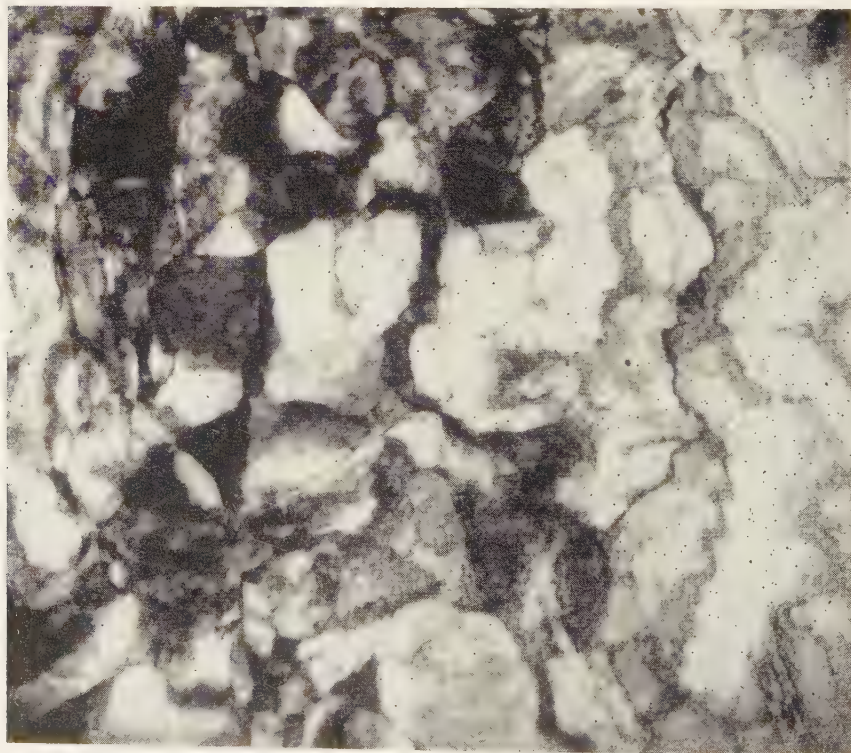


Fig. 2. Tungsten annealed at $1,300^{\circ}\text{C}$ for 15 minutes. ($\times 6,000$)

cutting out a portion for examination in the prototype M-V. E.M. 6 electron microscope. Annealing treatments were always carried out in bulk specimens prior to electropolishing, and were performed *in vacuo* by passing a current through them, the temperatures being measured by means of an optical pyrometer.

ELECTRON MICROSCOPICAL OBSERVATIONS

As-received material

The as-received tungsten (Fig. 1) had a structure typical² of cold worked metal, containing regions with a very high density of dislocations. Although large misorientations were frequently associated with these regions, no clear grain boundaries were detected in the metal. It appeared as though the misorientations, associated with any grain boundaries presumed to be present before working, had been spread out over the regions of these dislocation clusters.

Tungsten annealed at temperatures up to 1,500°C

After annealing for 15 minutes at temperatures up to 1,500°C, the dislocation distribution became clearer the higher the annealing temperature. The dislocations became more ordered (Fig. 2) and eventually arranged themselves in sharp boundaries



Fig. 3. An array of nearly parallel dislocations seen as a subgrain boundary in tungsten. Annealed at 1,500°C. ($\times 96,000$)

delineating equi-axed subgrains of about $2\ \mu$ diameter. At this stage only small misorientations ($\leq 2^\circ$) of the lattice were detected.

Many of these boundaries were inclined at a small angle with the film and were therefore resolvable. One of the most common types observed is that shown in Fig. 3, consisting of an array of nearly parallel dislocations, presumably a tilt boundary. Other arrays observed are shown in Figs. 4 and 5. The existence of these networks confirms that the reaction

$$\frac{a}{2} \begin{matrix} 111 \\ 2 \end{matrix} + \frac{a}{2} \begin{matrix} \overline{111} \\ 2 \end{matrix} \rightarrow a \begin{matrix} 001 \end{matrix}$$

occurs in tungsten as well as other body-centred-cubic metals^{2,3}. A feature of many of the boundaries is the close spacing ($\sim 100\ \text{\AA}$) of the dislocations resolved corresponding to misorientations of about 2° .

Tungsten annealed above $1,500^\circ\text{C}$

Recrystallised grains were first observed in specimens annealed at $1,500^\circ\text{C}$ (Fig. 6).



Fig. 4. Hexagonal array of dislocations in tungsten. Annealed at $1,500^\circ\text{C}$ for 2 h. ($\times 54,400$)

generally they were characterised by a much larger size than the polygonised grains, relatively smoother outline and comparative freedom from dislocations. As the annealing temperature was increased, the number of these recrystallised grains increased, until at about 1,900°C almost the whole specimen consisted of such grains.

Polygonisation was not complete before recrystallisation commenced, since areas of disordered dislocations could be found within 1 mm of some of the recrystallised grains (as observed by BOLLMANN⁴ in nickel). Further close examination led to the conclusion that it would be difficult, if not impossible, to distinguish between the smaller recrystallised grains and polygonised subgrains. For example, some of the subgrains in Fig. 7 seem to be well on the way to acquiring the characteristics of recrystallised grains; in addition it can be seen that the boundary of the recrystallised grain running down one side is not truly smooth but bends quite sharply where it meets the sub-boundaries.

GENERAL OBSERVATIONS

The as-received tungsten was ductile at room temperature and since the electron microscope work showed that it contained a high density of dislocations ($\sim 10^{11}/\text{cm}^2$),



Fig. 5. Tungsten annealed at 1,500°C. ($\times 31,000$)

many of which were in confused clusters, it was concluded that the material was in a "cold worked" state; *i.e.* the final working processes had been carried out well below the recrystallisation temperature. The tungsten began to lose its ductility after annealing at temperatures above about $1,100^{\circ}\text{C}$, and after annealing at or above $1,500^{\circ}\text{C}$ it was completely brittle. This corresponded with the gradual ordering of dislocations into low-angle boundaries (polygonisation) on annealing above $1,100^{\circ}\text{C}$ and the first signs of recrystallisation at $1,500^{\circ}\text{C}$.

Diffraction pictures were taken from the specimens and it appeared that in the polygonised specimens there was a strong preferred orientation, $\{100\}$ planes tending to be parallel to the plane of the foil. More scatter was observed in the cold worked specimens; the preferred orientation did not appear to exist in the recrystallised specimens. These observations agree with reports that the rolling texture of body-centred-cubic materials is $(001) [110]$, which persists after low temperature annealing⁵.

Although observations on the ductility of the tungsten were qualitative, being made by bending the specimens, the fractures of the less ductile specimens were of considerable interest. Those annealed below $1,500^{\circ}\text{C}$ always fractured on planes at 45° to the length of the tape, indicating cleavage on $\{100\}$ planes. Specimens which were recrystallised by annealing above $1,500^{\circ}\text{C}$ showed no such regularity. It was also observed that after a low temperature anneal (below $1,500^{\circ}\text{C}$) some parts of a specimen were ductile whilst other parts were very brittle. This effect was not caused by tem-



Fig. 6. Tungsten annealed at $1,500^{\circ}\text{C}$. ($\times 10,500$)

temperature gradients in a specimen, since sometimes a brittle region would lie on either side of a ductile region.

DISCUSSION

Metallography

Using conventional metallographic techniques it is very easy to etch low-angle sub-boundaries in tungsten⁶⁻¹⁰. If structures are very fine, as in the early stages of recrystallisation, this could lead to confusion between low-angle sub-boundaries and grain boundaries. As can be seen from our observations, the distinction may be important since recrystallisation appears to occur by growth of polygonised sub-grains already present, rather than the formation of fresh nuclei.

For example, in the work of SWALIN AND GEISLER¹¹ on the recrystallisation of tungsten, it is difficult to determine from some of their photographs whether recrystallisation or polygonisation is occurring. After low temperature anneals they obtained a grain size of about 2μ , which seems very stable; after a higher temperature anneal much larger grains were observed. For pure tungsten the temperature at which these occurred was much the same as in our work (their fine structure persisted up to $1,565^{\circ}\text{C}$) and it seems reasonable to conclude that they were observing polygonisation in the specimens annealed at low temperatures.

Because of the clarity with which this polygonised structure is revealed by transmission microscopy and the possibility of identifying precipitates with the selected



Fig. 7. Tungsten annealed at $1,600^{\circ}\text{C}$. ($\times 10,500$)

area diffraction technique it appears that this technique could be used to study the mechanism of the control of recrystallisation in tungsten by the use of various additions.

Ductility

Tungsten has appreciable ductility at room temperature when in two forms:

- (a) Heavily "cold" worked, *i.e.* worked below its recrystallisation temperature.
- (b) Single crystals of various purities produced by various techniques (zone melting^{6,12}, vapour deposition¹ and recrystallisation¹). However, in the recrystallised state it is extremely brittle.

From the present observations it appears that the principal feature which the ductile forms have in common is an absence of clear grain boundaries. It thus seems reasonable to attribute the brittleness of tungsten to grain boundaries. On this basis it is possible to account for the variation in ductility along the length of our polygonised specimens if it is assumed that either a few widely spaced grain boundaries do occur or that some of the polygonised boundaries have properties characteristic of grain boundaries. The low-angle boundaries are not likely to be sources of brittleness since many of the ductile single crystals contain such boundaries^{7,8,9}.

Such a correlation between the presence of grain boundaries and brittleness in tungsten would not be surprising if the fracture was entirely intergranular, possibly being associated with films of impurity at the boundaries. However, several observations suggest that this is not the case; for example,

- (a) the polygonised samples of the present investigation fractured by cleavage;
- (b) BECHTOLD¹³ and SHEWMON¹⁴ have observed considerable amounts of cleavage fracture in tungsten samples. It thus seems likely that in sufficiently pure tungsten most of the fracture occurs by cleavage although it is initiated at a grain boundary, as has been found in some samples of fine-grained molybdenum¹¹.

The initiation of fracture at a grain boundary suggests the presence of a precipitate acting as a stress concentrator. In the present study we have not found any evidence for the existence of precipitates, although it seems likely that they may exist in less pure tungsten. In this connection it is noteworthy that OLDS AND RENGSTORFF¹⁵ found evidence for a precipitate in molybdenum, a similar metal to tungsten, only at impurity levels above those at which considerable embrittlement occurred.

CONCLUSIONS

(a) Transmission electron microscopy is a useful technique in the study of the annealing of tungsten and its use could be extended to study the influence of additions on the recrystallisation process.

(b) There appears to be some evidence that the fracture of tungsten can be initiated at grain boundaries and propagated by cleavage.

(c) The recrystallisation of tungsten occurs by the growth of polygonised subgrains.

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III. Oxidation and Protection

OXIDATION MECHANISMS OF NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN

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SUMMARY

From published observations on the behaviour during oxidation of the four metals considered and from the properties of the oxides formed, the probable mechanism of oxidation is discussed. The known effects of alloying elements are dealt with in the light of this mechanism, and some consideration is given to other possibilities of improving oxidation resistance by simple alloying.

It is only quite recently that oxidation theory has begun to have some impact on the development of oxidation-resistant alloys for practical uses. Generally, this development has resulted from empirical approaches, which are, of course, very uneconomical. The reason for disregarding in practice the implications of theory is that our understanding of the mechanism of the oxidation of alloys is still meagre and advancing rather slowly.

The first practical successes have been obtained with metals for which the Wagner mechanism of oxidation applies in the temperature range of interest, that is where coherent oxidation films are formed in which the diffusion of ions is rate-determining. In these cases the film thickness (ξ) grows with time (t) according to a parabolic equation

$$\xi^2 = k_p t \quad (1)$$

where k_p is a constant. Since the compounds formed at the surface of metals are generally semi-conductors for which the diffusion mechanism has been elucidated in detail by C. WAGNER (see ref. 1), it is, in principle, possible to change the defect structure of the film by the addition of suitable alloying elements, or to form new films, in such a way as to reduce the diffusion rate in the film, and thus to increase the oxidation resistance of the metal.

OBSERVATIONS

Diffusion-controlled oxidation is, however, only one of several possible oxidation mechanisms, but the others are as yet less well understood. The progress of oxidation with time has frequently been studied for the four metals under review, by determining for example the weight increases in air or oxygen: niobium²⁻⁷, tantalum^{2,6,8,9,10,20},

niobium¹¹⁻¹⁵, tungsten^{11,16-19}. There is surprisingly good agreement on the types of time laws observed at various temperatures, showing that the shapes of the $\xi - t$ curves are well reproducible. The results are summarized in Table I. It is seen that parabolic oxidation (eqn. 1) occurs only at intermediate temperatures. As the temperature is raised (or the time of exposure extended) initial parabolic oxidation becomes linear. At still higher temperatures oxidation is linear throughout and is represented virtually entirely by the equation

$$\xi = k_1 t \quad (2)$$

TABLE I

TIME LAWS OBSERVED FOR THE OXIDATION OF NIOBIUM, TANTALUM, MOLYBDENUM AND TUNGSTEN IN AIR OR OXYGEN

Metal	100°	300°	500°	700°	900°	1,100°	1,300°C
Nb		par par	par-lin	lin	lin	accel.	asym
Ta	log inv. log	par	par-lin	lin	lin	delayed	
Mo		par	par-lin	par-lin	lin	lin	
W			par	par	par-lin	par-lin	par-lin

log = logarithmic oxidation
 inv. log = inverse logarithmic oxidation
 par = parabolic oxidation (usually after some initial deviation)
 par-lin = parabolic oxidation turning linear after a certain time
 lin = linear oxidation
 accel. = accelerated oxidation, *i.e.* faster than linear
 asym = asymptotic oxidation

At relatively low temperatures a logarithmic or an inverse logarithmic relationship has been found⁸ to fit the experimental results for tantalum. The corresponding rate equations are as follows

$$\xi = \xi_0 \ln t - C \quad (3)$$

$$1/\xi = A' - B' \ln t \quad (4)$$

respectively, where ξ_0 , C , A' and B' are constants.

In the temperature range, 220°–400°C, the results obtained with tantalum could also be represented empirically by a cubic relationship^{9,20}

$$\xi^3 = k_c t \quad (5)$$

At 330°C the surface films on niobium and tantalum are essentially amorphous²¹ and consist of Nb₂O₅ and Ta₂O₅ respectively, but after prolonged oxidation new patterns appear indicating the presence of suboxides at the metal-oxide interface. The sub-oxides decompose at about 400°C, and the X-ray patterns of the pentoxides become sharp at about 500°C²¹. In this temperature range, 300–500°C, the oxide films formed during moderate exposures are adherent and apparently pore-free, exhibiting bright temper colours²⁰. At 500°C, in the parabolic-linear transition range, small blister-like cracks start

forming and increase in number with time until their density is quite high⁷. With tantalum, slightly lenticular platelets of Ta_2O_5 (0.002 mm in thickness) extend into the metal²³. Above 500°C spalling and cracking become quite pronounced^{3,22} and at 800°C the oxidation product on tantalum decomposes into a white powder²⁰. At 1,000°C the scale on niobium seems to become more compact⁵, and at 1,250°C a coherent layer is formed which is, however, non-adherent and easily flakes off at the slightest provocation⁶.

The picture is somewhat different for molybdenum and tungsten. The surfaces remain bright¹⁶ up to 200°C and 300°C respectively and then temper colours appear. Two suboxides thought to have intermediate compositions between MoO_2 and MoO_3 have been found¹² at 570°C beneath an outer layer of MoO_3 . Above 550°C, MoO_3 begins to evaporate noticeably¹². Above the melting point of MoO_3 (795°C) oxidation is accompanied by a total loss in weight^{14,16} and the trioxide condenses in the cooler parts of the apparatus where it can be identified⁶. The volatility of WO_3 is much less, but becomes noticeable at temperatures above 850°C⁴⁷. Above 700°C WO_3 forms a yellow powdery outer layer^{16,19} of high porosity^{19,24} on oxidized tungsten. Underneath the porous trioxide layer there is a dense, thin, dark blue, adherent layer¹⁹ of uncertain composition, probably some intermediate oxide of tungsten.

PROPERTIES OF OXIDES

In order to discuss the observations summarized above, some properties of the surface compounds may be assessed. Although there have been some studies of the kinetics

PROPERTIES OF THE OXIDES OF Nb AND Mo

Compound	Remarks	Structure	Lattice constants (Å)	Moh. (°C)
Nb		b.c.c.	3.29	
Nb ₄ O		tetrag.(interst.)	3.35; 3.24	
NbO	25% lattice sites vacant	cubic: NaCl	4.21	
NbO ₂		≈ rutile	4.77; 2.96	
Nb ₂ O ₅ α	Metastable	orthorhombic	6.19; 3.65; 3.94	
Nb ₂ O ₅ β		monoclinic	21.34; 3.82, 19.5; 120.3°	
Ta		b.c.c.	3.30	
Ta _x O		tetrag.(interst.)	3.35; 3.25	
Ta ₄ O		orthorhomb.(interst.)	3.59; 3.26; 3.19	
TaO ₂	Metastable	tetrag: rutile	4.71; 3.07	
Ta ₂ O ₅ α	Stable < 1350°C	orthorhombic	6.20; 3.67; 3.90	
Ta ₂ O ₅ β	Stable > 1350°C	(triclinic)		
Mo		b.c.c.	3.14	
MoO ₂		monoclinic		
Mo ₄ O ₁₁		orthorhombic	24.4; 5.45; 6.72	
Mo ₉ O ₂₆	Stable < 650°C			
Mo ₈ O ₂₃	Stable > 650°C			
MoO ₃		orthorhombic	3.95; 13.9; 3.68	
W		b.c.c.	3.16	
WO ₂		monoclinic	5.56; 4.88; 5.55; 118.9°	
W ₄ O ₁₁		monoclinic	18.32; 3.79; 11.04; 115°	
W ₁₀ O ₂₉		~ ReO ₃		
WO ₃	Stable < 700°C	monoclinic	7.29; 7.52; 3.84; 90.9°	
WO ₃	Stable > 750°C	tetrag.	5.25; 3.92	

o = volume ratio disprop. = disproportionates dec. = decomposes () = uncertain

of the reaction of nitrogen with niobium^{2,5} and tantalum², the nitrides are of little importance in air-oxidation. The oxides are by far the most important surface compounds.

Some physical and physico-chemical data of the oxides of the four metals under review are listed in Table II. Essentially, these values have been taken from previous assessments of the present authors^{1,25}, but further information on the thermochemical data of niobium oxides^{26,27}, tungsten oxides²⁶, and molybdenum oxides²⁸, and on the structure of niobium and tantalum suboxides^{21,29} has been added.

There has been some argument on how many and which modifications of niobium pentoxide are stable and are formed during the oxidation of niobium^{4,22,30,31,49}, it appears, as happens so often, that the differences in energy between the various modifications are minute, and that their formation may consequently be affected by secondary influences such as experimental conditions and presence of impurities. The exact structural nature of the pentoxide is most probably not significant for the oxidation mechanism of niobium.

MECHANISM

Although there are some differences in the oxidation of the four metals under review, the sequence of the time-laws (Table I) is so similar that it is probably justifiable to assume the same oxidation mechanism for all four, and therefore to discuss them together.

Between 50° and 300°C first the logarithmic and then the inverse logarithmic laws

MOLYBDENUM AND TUNGSTEN

Type of conductor	ΔH_a (kcal/mole O ₂)	S_{298} (cal/°mole)	Homogeneity range	M.p. (°C)	B.p. (°C)
Met. (Met.)	0	8.73	log at. % O = 2.38 — 2650 T ⁻¹	2,468	4,400
		(11.5)	NbO _{0.98-1.00}	1,945	—
	190.9	13.03	NbO _{2.00}	1,915	—
n-type	182.1	32.8	NbO _{2.43-2.50} (980°C)	1,490	dec.
Met.	0	9.92	log at. % O = 1.76 — 2000 T ⁻¹	2,990	6,100
n-type	(200)			—	—
	198.0	34.2	TaO _{2.35-2.50}	1,785	—
Met.	0	6.83	0.03 at % O (1,100°C)	1,872	5,550
	139.5	17.05	MoO _{1.97-2.08}	2,600	disprop.
Met.	120.8	83.6	MoO _{2.65-2.75}	—	disprop.
n-type	118.8	18.6	MoO _{2.95-3.00}	795	disprop.
Met.	0	8.2			1,400 (MoO ₃) ₃
Met.	140.9	(19.0)			disprop.
Met.	(135.3)		WO _{2.65-2.72}		disprop.
	(134.5)				disprop.
n-type	134.1	19.9	WO _{2.95-3.00}	—	—
				1,473	> 2,000

seem to apply⁸. In these cases the oxidation mechanism suggested by CABRERA AND MOTT³² and amplified by HAUFFE AND ILSCHNER³³ should be applied. A very thin oxide film on a metal adsorbs oxygen at its surface, and electrons pass through the film from the metal to the adsorbed surface layer. In this way a very strong electric field is set up which pulls the ions (cations or anions) across the film. Depending on whether the passage of electrons or ions is rate-determining, one obtains a logarithmic (eqn. 3) or inverse logarithmic (eqn. 4) relationship between the increase in thickness and the time. According to HAUFFE AND ILSCHNER³³, eqn. 3 would be expected to apply to extremely thin films, and to change to the inverse logarithmic relationship as the film thickens. This is exactly what happens with tantalum, so that the proposed mechanism would appear to be satisfactory. There is also other evidence for the validity of the CABRERA-MOTT-HAUFFE-ILSCHNER mechanism (*e.g.*, ref. 34). There is, however, a recent new suggestion by UHLIG³⁵ according to which the transfer of electrons across the metal-oxide interface, which involves the work function, may be rate-determining, a suggestion leading to two successive logarithmic growth laws which may be applicable to substantial oxide thicknesses of the order of 10,000 Å, or to a logarithmic followed by a cubic law. GRIMLEY AND TRAPNELL⁵¹ have also considered the rate laws for thin films in terms of chemisorption of the oxidising gas at the surface.

The possibility of applying a formal cubic relationship to the oxidation of tantalum is very doubtful. However, several attempts have been made to derive a cubic law^{32,35,36} and even apply it to tantalum³⁷. Objections to the latter have already been raised¹, and it is not yet clear whether the models on which the derivations were based are really applicable, or whether some secondary effect, *e.g.*, an "ageing" of the oxide film, does not produce an apparent cubic relationship.

More likely, parabolic oxidation follows the inverse logarithmic type as the temperature is raised (Table I). At this stage, the oxidation rate becomes diffusion controlled, the driving force being no longer the electric field but the concentration gradient as in the Wagner mechanism. Most of the lower oxides are metallic conductors in which diffusion rates are probably fast, and the slowest, rate-determining, diffusion takes place in the highest oxides, which are all cation-excess, or rather anion-deficit, conductors. This has been concluded from conductivity measurements^{12,13,22,39} and was confirmed for MoO₃^{12,13} and Nb₂O₅⁷ by marker methods. The apparent anion excess observed by ARGENT AND PHELPS⁵⁰ for Nb₂O₅ formed on commercial niobium is difficult to explain, but it is possibly associated with the amorphous nature of the oxide at low temperatures.

For *n*-type semi-conducting surface layers the parabolic oxidation rate should be independent of the oxygen pressure. This has indeed been observed for tantalum²⁰ at 450°C up to 100 mm Hg. It has also been shown at higher pressures for niobium⁴⁰ below 500°C, molybdenum⁴¹ below 550°C and tungsten⁴⁷ up to 700°C.

The parabolic oxidation at intermediate temperatures is thus most probably controlled by the diffusion of O⁻ ions through the film consisting mainly of the highest oxide, and new oxide forms at the metal-oxide interface. All the metals under review have another feature in common in that the volume ratios for the highest oxides are exceptionally large: 2.45-3.5 (Table II). Because of this the newly formed oxide expands against the resistance of the existing oxide layer, and severe biaxial stresses develop which eventually lead to rupturing of the film. This is obviously the mecha-

nism^{7,22} (at least for niobium and tantalum) leading to the parabolic time curves turning into linear ones, at temperatures between 500° and 700°C (Table I). In the case of tantalum, its conversion into oxide has been shown^{10,23} to occur by the nucleation and growth of little plates along the {100} planes of the b.c.c. metal. Simultaneously, of course, oxygen dissolves in tantalum (and niobium) and the depth of penetration can be estimated by micro-hardness tests^{5,10}.

This mechanism probably applies to molybdenum and tungsten as well as to niobium and tantalum. WEBB, NORTON AND WAGNER¹⁹, have pointed out the strong adherence and adherence of the inner oxide layer on tungsten. Its rate of formation is presumed to be inversely proportional to its thickness. It seems to transform to the porous outer oxide at a constant rate and therefore reaches a limiting thickness within a short time. By combining the rate laws for the two processes WAGNER *et al.* arrive at an equation which represents the actual observations. Thus the parabolic-linear oxidation at intermediate temperatures may have a somewhat different cause for niobium and tantalum on the one hand, and tungsten and molybdenum on the other.

As the temperature is raised further, the parabolic portion of $\xi-t$ curves is suppressed and oxidation becomes virtually linear, that is oxygen penetrates the porous and cracked surface layer and reaction takes place at the substantially unprotected metal surface.

The asymptotic $\xi-t$ curve observed on niobium at 1,250°C⁶ may be caused by a separation between the metal and the non-adherent and, owing to the high volume ratio, strongly stressed Nb₂O₅ layer. Such layers although highly protective are, of course, mechanically very weak.

EFFECT OF ALLOYING ELEMENTS

An important aim of the attempts to elucidate the oxidation mechanism is, of course, the development of oxidation-resistant alloys for technical purposes. Since the mechanism of oxidation of the metals under review is somewhat involved, it is not easy to make suggestions for improving the oxidation resistance by alloying. Where the Wagner mechanism applies it is usual to try to "fill the holes" in the oxide. That is, for metals having *n*-type conducting oxides it is possible to make metallic additions that have a higher valency, a higher affinity for oxygen, and a smaller radius in the ionic form¹, so that the added element dissolves in the form of ions in the oxide of the base metal, and reduces the number of cations per anion and thus the number of anion deficiencies such as vacancies in the anion lattice.

The Wagner mechanism appears to apply exclusively only below about 500°C for the present metals. Because of the high valencies of these metals the choice of beneficial metallic additions is very limited. Molybdenum, tungsten and, possibly, chromium might be beneficial with niobium and tantalum, but owing to the lower affinity for oxygen no substantial improvement would be expected. Results of oxidation tests on alloys below 500°C do not seem to be available, but the good effect of 5% molybdenum (but not of tungsten) on the oxidation of niobium⁴² at higher temperatures is of interest in this connection.

Most of the experimental measurements on alloys have been carried out at 800°-1,000°C; since many of these have been made using niobium as a base, much of the following discussion will deal with alloys of this metal. Titanium, zirconium and

tantalum, after an initial worsening, all have a beneficial effect on the oxidation resistance of niobium at higher concentrations^{42,43}. It may be suggested that the beneficial effect is due to a Wagner mechanism "in reverse". The three metals mentioned have a higher affinity for oxygen than niobium, and would therefore be oxidised preferentially. When these metals are present in sufficient concentration in the alloy, coherent films of TiO_2 , ZrO_2 or Ta_2O_5 may be formed. These three oxides are also *n*-type semi-conductors with vacant sites in the O^{2-} lattices, and since they would also be saturated with Nb^{5+} ions the number of vacant sites would be considerably reduced. In addition, the volume quotients of at least TiO_2/Ti and ZrO_2/Zr are considerably smaller than that of $\text{Nb}_2\text{O}_5/2 \text{ Nb}$ and the oxide layers thus much less prone to cracking.

It is, of course, possible to form double oxides on binary alloys, or more complex oxides on multi-component alloys. It is usually not possible to make reliable predictions concerning their protective roles because not sufficient is known about their properties. It is of interest, however, that the oxide $6 \text{ ZrO}_2 \cdot \text{Nb}_2\text{O}_5$ formed on niobium-zirconium alloys (approximately 50/50 at. %) does not spall on cooling, and is protective for a few hours at $1,000^\circ\text{C}$, but a transition to a more rapid oxidation rate then occurs⁴⁸. The addition of 5 at. % titanium has been stated to be effective in suppressing this transition, and an improvement in oxidation resistance (based on a 10 hour exposure in air at $1,000^\circ\text{C}$) of a factor of ten over unalloyed niobium is obtained.

Similar considerations to the above apply to additions to niobium of aluminium and beryllium which have beneficial effects⁴². In these cases the affinities for oxygen are again higher and the oxides are of the *n*-type, but the ionic radii are smaller than that of Nb^{5+} so that the latter is unlikely to be dissolved in BeO and Al_2O_3 to any noticeable extent. The improvement in oxidation resistance of niobium is therefore less than for zirconium and titanium additions. Chromium has about the same affinity for oxygen as niobium; otherwise its relevant properties resemble those of zirconium and titanium. The lower oxygen affinity may explain why chromium additions to niobium are effective only above about 20 at. %⁴².

Although these considerations seem to explain the beneficial effect of some alloying elements on the oxidation resistance of niobium, they are not altogether encouraging since the basic mechanism of preferential oxidation is difficult to control. The improvements may fail to be observed under different practical conditions (strong initial oxidation, for instance). Other ways of improving the oxidation resistance by alloying on the basis of the apparent mechanism should be considered.

The main difficulty with the metals under consideration is the magnitude of the stresses developed in the surface films owing to the high volume ratios, and an obvious objective would be to try to reduce these ratios. This can probably be done by "diluting" the alloy surface with an inert metal, or, since this would be rather expensive, with a metal of much lower oxygen affinity. Possibly, the beneficial effect of nickel on the oxidation rate of molybdenum⁴⁴ is due to such a reduction in volume ratio. Nickel and cobalt, however, somewhat decrease the oxidation resistance of niobium^{6,42}, but this conclusion is based on results for additions up to 5 at. % only. Owing to the relatively small size of the Ni and Co atoms larger concentrations would be required to produce the desired effects. The ion of the added metal also should be large to make it less soluble in the surface oxide. Copper may be a potential addition of the required nature.

On the whole, the prospects for a sufficiently large improvement in the oxidation resistance of the metals under review are not promising. Attempts to achieve the desired improvements by coating the surfaces have therefore frequently been made (see, for example, ref. 45). The excellent oxidation resistance of MoSi_2 on molybdenum^{45,46}, for instance, was a result of this research. The discussion of protection, however, is outside the scope of this review.

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THE OXIDATION OF NIOBIUM-TITANIUM AND
NIOBIUM-MOLYBDENUM ALLOYS

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SUMMARY

The oxidation rates of several niobium-titanium and niobium-molybdenum alloys have been measured over a considerable range of temperature and the results may be understood in terms of the chemical and physical properties of the scales.

INTRODUCTION

Many workers¹⁻⁷ have investigated the oxidation of niobium, and the relevant features of its behaviour are described in Table I. A possible scheme to explain these results is given below. It assumes that oxygen is adsorbed on the outer oxide surface and that it subsequently dissociates and is incorporated in the scale. A detailed description of this type of adsorption process is given by STRINGER AND COWGILL⁸.

200-400°C

The potential sites for oxygen adsorption on the oxide surface are all occupied, giving a pressure-independent oxidation rate. The rate-controlling process is the diffusion of anions through a coherent oxide layer and a parabolic growth law results.

400-450°C

The oxide layer reaches a limiting thickness at which it can no longer stand the mechanical stresses due to the high volume ratio of the oxide, and the scale cracks. The rate-controlling process is the diffusion of anions through a coherent oxide layer to the surface of the metal, but this layer is of virtually constant thickness. An adsorbed layer of oxygen completely covers the oxide surface and a linear pressure-dependent oxidation rate results.

450-600°C

The surface of the oxide is no longer saturated with adsorbed oxygen and the temperature dependence of the rate of oxidation decreases. Diffusion is still the rate-controlling process and thus the rate of oxidation depends on the square root of the oxygen pressure. The outer scale breaks down to a fine powder owing to the large

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TABLE I
CHARACTERISTIC FEATURES OF THE OXIDATION OF NIOBIUM

	Temperature range, °C				
	250°-400°	400°-450°	450°-600°	600°-675°	675°-850°
Growth law	parabolic	parabolic changing to linear	parabolic changing to linear	linear	linear
Temperature dependence of oxidation rate (0.038 cm thick specimen)	+ve	+ve	+ve	-ve	+ve
Pressure dependence	Independent	Independent	p ¹	p ¹	p ¹
Oxide type	amorphous + $\alpha\text{Nb}_2\text{O}_5$	Independent $\alpha\text{Nb}_2\text{O}_5$ + amorphous (broad lines)	p ¹ $\alpha\text{Nb}_2\text{O}_5$ (broad lines)	p ¹ $\alpha\text{Nb}_2\text{O}_5$ (broad lines)	p ¹ $\alpha\text{Nb}_2\text{O}_5$ (sharp lines)
Oxide character	Adherent film showing temper colours	Adherent dark film	Cream oxide some spalling at temperature Particle size (1,000-10,000 Å)	Cream oxide slight spalling	Light grey oxide changing to dark grey with increasing temperature No spalling at temperature or on cooling
Deviations from stoichiometry (0.038 cm thick specimen)	Not known	Changes from anion deficient at 400°C to apparent cation deficiency at 450°C	Maximum specific surface 450°C Apparently cation deficient. Approaches stoichiometry at 550°C	Increasing anion deficiency	Anion deficient returning to stoichiometry at 800°C
					Not known

change in density consequent on the transformation of amorphous Nb_2O_5 to $x\text{Nb}_2\text{O}_5$ (a density change of 4.36 to 5.17 gm/cm³ at room temperature) and the increased surface area of the oxide partially compensates for the decreased adsorption per unit surface area. If approximately 50% of the surface sites were occupied the high surface area could account for up to 0.5% extra oxygen in the scale and the apparent oxygen deficiency observed by ARGENT AND PHELPS⁷. At temperatures above 550°C an increasing rate of diffusion of oxygen from the scale into the underlying metal gives an anion-deficient oxide.

500°–675°C

The surface area of the scales¹¹ and the adsorption per unit area decrease rapidly and give a decreasing rate of oxidation with increasing temperature. Adsorption becomes, for a short temperature range, the rate-controlling factor and gives a linear pressure dependence.

675°–850°C

The surface concentration of oxygen is no longer controlled by adsorption but depends solely on the oxygen concentration in the gas phase. Diffusion through the inner oxide layer once again becomes rate-controlling and the rate of oxidation depends on the square root of the oxygen pressure.

850°–1,400°C

By 850°C the underlying metal, in thin niobium specimens, is largely saturated with oxygen and the oxides are apparently much nearer to stoichiometry. The oxide formed above 850°C is $\beta\text{Nb}_2\text{O}_5$ and the temperature dependence of the oxidation rate increases. The subsequent acceleration noted by some workers at $\sim 1,150^\circ\text{C}$ could be due to the onset of conditions analogous to combustion involving a considerable rise in the temperature of the specimen. KLOPP, SIMS AND JAFFEE⁵ report that at 1,400°C the heat of reaction was sufficient to melt the niobium metal.

The addition of alloying elements to niobium can vary the oxidation behaviour in several ways, for example, by

1. Altering the rates of diffusion through the scale.
2. Forming phases other than Nb_2O_5 in the scale.
3. Altering the plasticity of the scale.
4. Varying the lattice parameters of the scale and underlying metal and thus altering the volume ratio.
5. Altering the rates of diffusion of oxygen into the metal.

The effect of variations in the lattice parameters of the scale and metal is likely to be of least importance since most alloying elements will alter both parameters in the same direction.

A preliminary survey of the rates of oxidation of several alloys showed reasonable agreement with previous work^{9,10} and a more detailed study was then made of the effect of additions of titanium and molybdenum.

EXPERIMENTAL

The alloys were made from niobium containing 0.25% tantalum, 0.01% carbon, 0.01%

oxygen and negligible amounts of other impurities, sintered molybdenum (total impurities 0.2%) supplied by Murex Ltd. and titanium sponge (metallic impurities 0.3%) supplied by Imperial Chemical Industries.

Alloys were melted in a tungsten electrode argon arc furnace using a pressure of $\frac{1}{2}$ atmosphere Saturn Industrial Gases 99.99% Argon. The furnace atmosphere was gettered by melting a piece of niobium and then 20 g buttons of the alloys were melted and turned over at least three times. Each button was given a short high temperature anneal by reducing the arc current to a minimum and continuing to heat the specimen for a further five minutes. Specimens (2×1 cm), blanked from 0.038 cm sheet rolled from these buttons, were used in the as-rolled condition for the oxidation tests.

Two alloys containing molybdenum were homogenised for 25 h at 1,650°C prior to rolling. Specimens blanked from these sheets showed similar rates of oxidation to specimens of similar compositions which had only received the short heat treatment in the arc furnace.

The progress of oxidation was followed by measuring the weight gain with a pyrex spring balance. Changes in weight of 0.2 mg could easily be detected. The specimens were suspended inside an electrically heated tube furnace (internal diameter of tube = 3 cm) by means of a silica rod attached to the calibrated pyrex spring. Any oxide that spalled from the specimen was collected in a platinum dish attached to the suspension. Temperatures were controlled to $\pm 2^\circ\text{C}$ and a platinum/platinum 13% rhodium thermocouple, located near the specimen, was used to determine its temperature. Oxygen was passed through the furnace from top to bottom at a rate of 1 litre/minute.

Oxides were analysed for titanium by fusing with potassium bisulphate, dissolving in a mixed sulphuric and tartaric acid solution and determining the titanium colorimetrically after the addition of phosphoric acid and hydrogen peroxide. Molybdenum contents were determined colorimetrically on sulphuric acid solutions after the addition of oxalic acid and ammonium thiocyanate.

X-ray photographs for identification purposes were obtained with a Unicam 19 cm camera using copper radiation.

RESULTS

The weight-gain/time curves were linear at all temperatures after an initial non-linear period whose duration varied with temperature and alloy content. Variations in the linear rate constants from duplicate tests were no greater than the uncertainty in determining the constants.

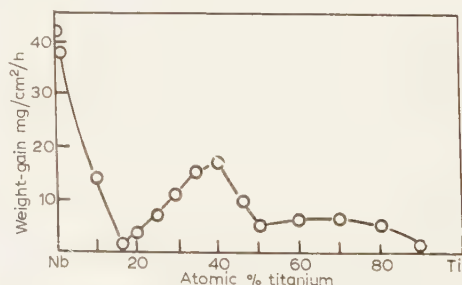


Fig. 1. Weight-gain oxidation rates for niobium-titanium alloys exposed at 1,050°C to moist air. (Saturated with water at room temperature.)

At the beginning of this work a survey was made of the oxidation behaviour of a series of alloy systems; the results are given in Table II. The trends shown by the data are in agreement with other surveys^{9,10}. Titanium, vanadium and molybdenum reduce the rate of oxidation of niobium, whereas small additions of zirconium appear to be particularly harmful.

TABLE II
OXIDATION RATES FOR NIOBIUM ALLOYS EXPOSED IN MOIST AIR

Alloy at. %	Oxidation rate mg/cm ² .h			
	550°C	700°C	800°C	1,020°C
Pure Niobium	3.7	7.4	22.8	38.0
1 Tantalum	5.6	6.1	28.3	14.6
5 Tantalum	5.6	6.1	28.3	14.6
10 Tantalum	3.7	6.7	28.3	25.6
20 Tantalum	5.6	5.6	19.5	36.0
1 Vanadium	3.4	7.0	32.0	9.9
5 Vanadium	1.4	1.0	3.7	7.0
1.7 Chromium	—	13.7	27.4	35.0
5 Molybdenum	—	—	0.9	4.3
1 Tungsten	3.3	—	6.0	17.7
1 Titanium	3.0	—	2.7	37.3
10 Titanium	1.0	0.7	2.1	13.7
20 Titanium	—	1.0	0.8	3.3
46 Titanium	—	—	1.0	9.2
1 Zirconium	—	8.4	33.8	50.0

A rather more detailed examination was made of the composition dependence of the oxidation rates of niobium-titanium alloys at 1,050°C. The results plotted in Fig. 1 show that alloys containing ~ 17% titanium oxidise at appreciably lower rates than the other alloys investigated. These results suggested that niobium-titanium alloys might be the basis for the development of more complex oxidation-resistant alloys and it was considered desirable to investigate in detail the temperature and composition dependence of their oxidation behaviour. A parallel investigation was carried out on niobium-molybdenum alloys.

Figs. 2, 3 and 4 show the temperature dependence of the oxidation rates of a series of niobium-titanium and niobium-molybdenum alloys as compared with pure niobium. Tables III, IV and V show the characteristics of the oxides.

At 450°C niobium-titanium alloys oxidise at lower rates than pure niobium and the extent of the improvement appears to depend on the concentration of titanium. However, by 550°C alloys containing less than 3.5% titanium have more rapid rates of oxidation than the pure metal. Between 600° and 700°C, alloys with less than 5.4% titanium show accelerated oxidation, whereas high concentrations of titanium reduce the rate of oxidation below that of pure niobium. Above 750°C all alloys show an improvement over pure niobium and up to 900°C this increases with the amount of titanium. At temperatures greater than 900°C a 25 at. % alloy oxidised at a greater rate than an alloy containing 18 at. % titanium.

TABLE III
OXIDE CHARACTERISTICS OF NIOBIUM-TITANIUM ALLOYS

Temp. (°C)	1-5 at. %	5-10 at. %	10-20 at. %
400-500	400: Thin black adherent film. 450: Cream oxide which spalls on cooling, leaving some oxide on metal surface		
500-700	Oxide goes from powdery cream to coherent yellow with increased Ti and temperature	Oxide goes from powdery cream through grey to a black adherent scale with increased Ti and temperature	Adherent black layer
700-1,100	A yellowish adherent scale changing to a thin grey film overlaying black surface. Above the allotropic change temp. a creamy crystalline oxide which spalls cleanly on cooling	Black adherent scale changing to a greyish powdery scale with increasing temp. for the low Ti alloys. Above the change point a creamy oxide cleanly spalling on cooling.	Dark grey oxide showing slight spalling at lower temperatures. Above allotropic point a creamy oxide which cleanly spalls on cooling

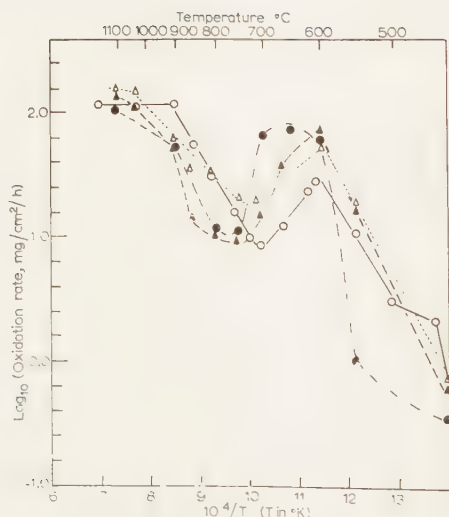


Fig. 2. Log_{10} (oxidation rate) plotted against $1/T$ for niobium-titanium alloys exposed to dry oxygen. Pure niobium $\circ$; 3.5 at. % titanium $\blacktriangle$; 1.6 at. % titanium $\triangle$; 5.4 at. % titanium $\bullet$.

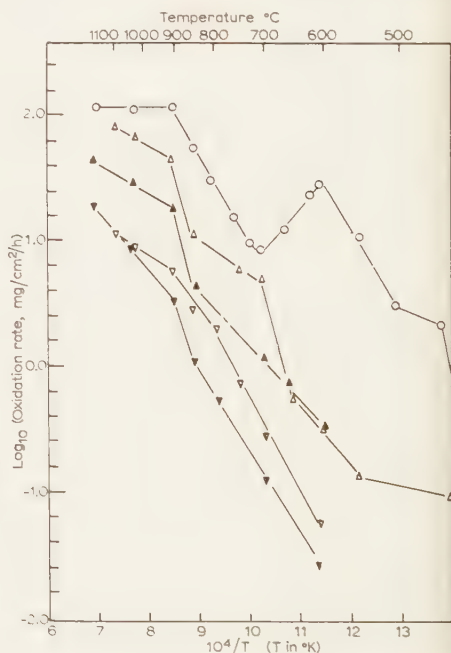


Fig. 3. Log_{10} (oxidation rate) plotted against $1/T$ for niobium-titanium alloys exposed to dry oxygen. Pure niobium $\circ$; 9.8 at. % titanium $\blacktriangle$; 6.6 at. % titanium $\triangle$; 18.0 at. % titanium ∇ ; 25.0 at. % titanium ∇ .

TABLE IV

OXIDE CHARACTERISTICS OF NIOBIUM-MOLYBDENUM ALLOYS

Temp. °C	0-1 at. %	1-3 at. %
400-500	400: Adherent greyish yellow oxide 450: Powdery yellow oxide	400: Adherent yellowish grey 450: Slight formation of powdery yellow oxide.
500-700	Yellow powdery oxide becoming more grey and coherent with increased Mo and temperature	A powdery yellow-grey oxide changing to a light black adherent oxide at higher temperatures and molybdenum contents.
700-900	Black adherent oxide becoming covered by a thin grey film at higher temp. Cream oxide above change point.	Black adherent oxide. Above change point a grey-cream oxide retained on cooling

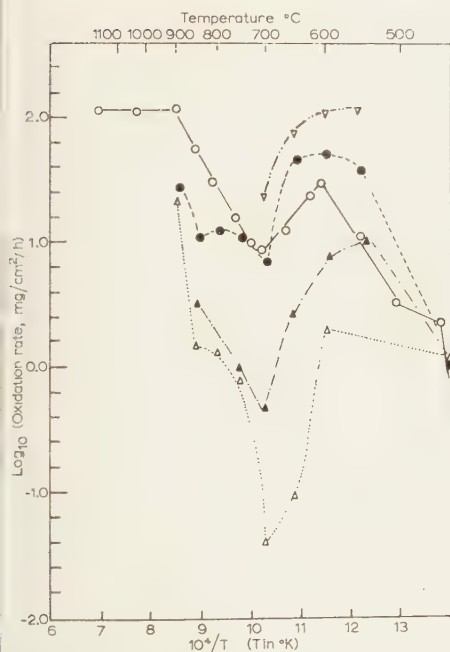


Fig. 4. Log_{10} (oxidation rate) plotted against $1/T$ for niobium-molybdenum alloys exposed to dry oxygen. Pure niobium $\circ$; 1.0 at. % molybdenum $\bullet$; 0.4 at. % molybdenum ∇ ; 1.9 at. % molybdenum $\blacktriangle$; 3.4 at. % molybdenum $\triangle$.

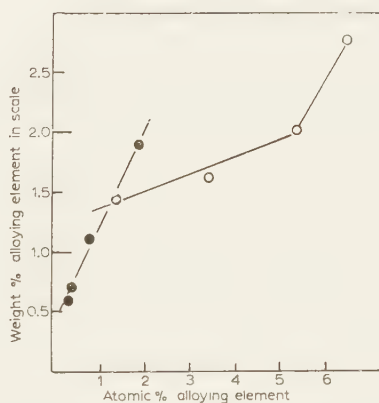


Fig. 5. The concentration of titanium and molybdenum in scales formed on various alloys at 600°C. $\circ$ Titanium alloys; $\bullet$ molybdenum alloys.

Niobium-molybdenum alloys oxidise more rapidly than pure niobium at temperatures between 450° and 550°C. At higher temperatures alloys containing greater than 1.9% molybdenum oxidise at significantly lower rates than pure niobium. 0.4 at. % and 1.0 at. % molybdenum alloys respectively showed accelerated oxidation up to 700°C and 650°C.

TABLE V
 X-RAY EXAMINATION OF SCALES

Composition Temp. °C	at. % Titanium			at. % Molybdenum		
	1.5	3.5	6.5	1	1.9	3.4
900	$\beta\text{Nb}_2\text{O}_5$	$\beta\text{Nb}_2\text{O}_5$	$\beta\text{Nb}_2\text{O}_5$ + trace cpd.	$\beta\text{Nb}_2\text{O}_5$	$\beta\text{Nb}_2\text{O}_5$	$\beta\text{Nb}_2\text{O}_5$
850				$\alpha\text{Nb}_2\text{O}_5$ + $\beta\text{Nb}_2\text{O}_5$		
800				$\alpha\text{Nb}_2\text{O}_5$	$\alpha\text{Nb}_2\text{O}_5$ + $\beta\text{Nb}_2\text{O}_5$	
750	$\alpha\text{Nb}_2\text{O}_5$		$\alpha\text{Nb}_2\text{O}_5$ + cpd.	$\beta\text{Nb}_2\text{O}_5$		$\beta\text{Nb}_2\text{O}_5$
700	$\alpha\text{Nb}_2\text{O}_5$		$\alpha\text{Nb}_2\text{O}_5$ + cpd.			
680					$\alpha\text{Nb}_2\text{O}_5$	
650						$\alpha\text{Nb}_2\text{O}_5$
600	$\alpha\text{Nb}_2\text{O}_5$	$\alpha\text{Nb}_2\text{O}_5$	$\alpha\text{Nb}_2\text{O}_5$ + cpd.			
550	$\alpha\text{Nb}_2\text{O}_5$		$\alpha\text{Nb}_2\text{O}_5$ + cpd.	$\alpha\text{Nb}_2\text{O}_5$	$\alpha\text{Nb}_2\text{O}_5$	$\alpha\text{Nb}_2\text{O}_5$

cpd. = $\text{TiO}_2 \cdot 3 \text{Nb}_2\text{O}_5$

Alloys containing titanium and molybdenum show marked differences in their behaviour at 700°C. The minimum in oxidation rates noticed for pure niobium is maintained and accentuated by molybdenum additions, whereas in the case of alloys containing titanium it becomes much less obvious.

An X-ray examination of the scales showed that

1. The improvement in oxidation resistance of alloys containing more than 6.6 at. % in the temperature range 550°–700°C is associated with the formation of $\text{TiO}_2 \cdot 3 \text{Nb}_2\text{O}_5$ in the scale.

2. Titanium has little effect on the apparent transition temperature from $\alpha\text{Nb}_2\text{O}_5$ to $\beta\text{Nb}_2\text{O}_5$.

3. Molybdenum progressively stabilises $\beta\text{Nb}_2\text{O}_5$ until it appears at 750°C for a 3.4 at. % alloy.

Analyses of scales formed on niobium–titanium alloys at 600°C show a rapid increase in titanium content at the alloy composition where $\text{TiO}_2 \cdot 3 \text{Nb}_2\text{O}_5$ was first observed. However, scales formed on niobium–molybdenum alloys show a smooth increase in their molybdenum content with the composition of the alloy (Fig. 5).

DISCUSSION

Niobium–titanium alloys

The oxide of titanium with the nearest stability to Nb_2O_5 is TiO_2 and the Ti^{4+} ion is also very similar in size to the Nb^{5+} ion (0.68 Å and 0.69 Å respectively). This suggests that titanium dissolves in Nb_2O_5 as Ti^{4+} and will thus tend to increase the number of anion defects and the rate of oxygen transfer through the scale. SIMS,

KLOPP AND JAFFEE⁹, however, have shown that the rate of diffusion of oxygen in niobium-titanium alloys is much less than in pure niobium. For example, the diffusion constant is reduced by a factor of ~ 20 for the 25 at. % alloy. The activation energy for diffusion is in this case 30,800 cal/mole as compared with 24,900 cal/mole for pure niobium. This will tend to reduce the rate of transfer of oxygen to the metal and thus decrease the anion deficiency in the scale. It seems likely that a balance between these factors and sintering determines the oxidation behaviour of the alloys. At low temperatures the rate of diffusion of oxygen into the underlying metal is reduced and the scale will tend to be much nearer to stoichiometry than that formed on pure niobium; apparently the influence of titanium dissolved in the scale is not sufficient to compensate for this effect. However, at higher temperatures the rate of diffusion of oxygen into alloys containing small amounts of titanium rises and an appreciable number of defects are formed in the scale. Titanium dissolved in the scale accentuates this effect and a rapid rate of oxidation results. Above 700°C marked sintering of the scale occurs and, for the thin specimens used in these tests, the scales return to stoichiometry as the oxygen content of the metal increases. These effects combine to give rates of oxidation lower than pure niobium. With high titanium contents diffusion of oxygen into the underlying metal is slow at all temperatures and the region of rapid oxidation is not apparent for titanium contents greater than 10 at. %. The influence of the fact that the activation energy for the diffusion of oxygen is greater in niobium-titanium alloys than in pure niobium is possibly demonstrated by the improvement in resistance to oxidation being more marked at low temperatures than at high temperatures. The allotropic change in Nb_2O_5 is associated with an inflexion in the oxidation rate/temperature curves for all the alloys and this is probably associated with the fact that the rates of diffusion of oxygen through the two allotropes are likely to differ even when there is titanium in solution.

Niobium-molybdenum alloys

The oxide of molybdenum with the nearest stability to Nb_2O_5 is MoO_2 and the Mo^{4+} ion (0.70 Å) is nearer in size to Nb^{5+} (0.69 Å) than the Mo^{6+} ion (0.62 Å). This suggests that molybdenum dissolves in Nb_2O_5 as Mo^{4+} . The data of SIMS, KLOPP AND JAFFEE⁹ suggests that the rate of diffusion of oxygen in niobium-molybdenum alloys is slightly greater than in pure niobium. Thus niobium-molybdenum alloys are likely to show rates of oxidation greater than pure niobium at low temperatures, where sintering is unimportant.

At temperatures up to 700°C low concentrations of molybdenum accelerate the rate of oxidation but at higher temperatures and high concentrations of molybdenum sintering of the scale is very marked. This is not surprising since molybdenum oxides have low melting points (*e.g.* MoO_3 795°C). Sintering of the scales greatly reduces their surface area and therefore the amount of adsorbed gas. At temperatures where surface adsorption is important this will contribute to the low rates of oxidation of the alloys but when this is no longer important ($> 700^\circ\text{C}$) the rates of oxidation will increase. The data at temperatures greater than 800°C are rather suspect since some MoO_3 may be formed and volatilised. However, the general impression is that the rates of oxidation increase very rapidly with increasing temperature and this may be associated with the formation of a partly liquid oxide.

CONCLUSIONS

The oxidation rates of niobium alloys depend on many factors but the most important appear to be:

1. The ease of formation of anion-deficient lattices and the influence of added elements on the diffusion of oxygen into the metal and through the scale.
2. The enhanced sintering of the scale owing to the presence of low melting point oxides.
3. The formation of mixed oxides which decrease the rate of oxygen diffusion through the scales.

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THE DEVELOPMENT OF OXIDATION-RESISTANT NIOBIUM ALLOYS

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SUMMARY

Various mechanisms, whereby the addition of an alloying element to niobium may influence the oxidation resistance, are examined in the light of previous experimental work; it is concluded that the effects observed are probably due to the combination of a number of factors. An account is given of systematic investigations into the oxidation resistance of an extensive range of ternary and more complex niobium alloys, containing from 9 to 25 atomic % titanium, which have succeeded in identifying ductile and refractory alloys showing oxidation rates at 1,100°C of about 1% of that of pure niobium metal.

INTRODUCTION

Increased attention has recently been paid to niobium as the possible base for a new series of materials for use at high temperatures. Conventional creep-resisting alloys are proving inadequate at temperatures above 1,050°C, but niobium retains a useful degree of strength in this temperature range. On the other hand, niobium oxidises rapidly above 1,000°C that in the pure or unprotected form it cannot be used in an oxygen-bearing environment at these temperatures.

It was the purpose of this investigation to examine the effect of alloying on the oxidation resistance of niobium, in order to develop alloys which could be used for structural applications under the above conditions. As the resultant materials were required to be tough and refractory, any alloying development which was found to be accompanied by a severe lowering of the creep-resistance or ductility was rejected.

THE MECHANISM OF NIOBIUM OXIDATION

When niobium is exposed to an oxidising atmosphere it is believed that, after the initial dissolution of a small percentage of oxygen¹, oxidation probably commences with the formation of one or all of the lower oxides of niobium^{2,3} (Nb_2O , NbO and NbO_2); but the presence of these oxides has not been conclusively established experimentally under all temperature and pressure conditions of oxidation. Moreover, it is clear that if present, these lower-oxides exist only as relatively thin layers and probably play a negligible part in the oxidation process at elevated temperatures.

The next stage is the formation of a preferentially-orientated layer of $\alpha\text{-Nb}_2\text{O}_5$, which subsequently recrystallises and becomes randomly-orientated. Further holding at the oxidation temperature results in the transformation of α to β Nb_2O_5 , the equilibrium phase¹ at all temperatures above room temperature.

During the growth of the Nb_2O_5 layer there is a change in its physical state un-

connected with the α to β transformation, the transformation of the scale from a black adherent dense phase into a white inadherent porous one.

The primary cause of the high oxidation rate of niobium is probably the large volume ratio of Nb_2O_5 to the metal from which it is formed. Owing to the dimensional restraint imposed by the metal, severe compressive stresses develop in the scale as it grows, causing periodic cracking³, which allows the physical penetration of oxygen.

While still sound, the scale is partially protective and if the scale could be modified by alloying, in order to increase the thickness which it attains before fracture, improvements in the oxidation resistance should result. Also, if alloying additions could be found that would reduce the diffusion rate of oxygen in the compact scale, the oxidation rate should again be decreased as the scale would take longer to reach the critical thickness for fracture.

THE INFLUENCE OF ADDED ELEMENTS ON THE MECHANISM OF NIOBIUM OXIDATION

Various factors which may influence oxidation resistance will now be examined in the light of published experimental findings.

The effects of many added elements vary with temperature; but the following discussion is primarily concerned with the reported behaviour between about 1,000°C and 1,200°C since this was the main range of interest in the present investigation.

The formation of oxides other than Nb_2O_5

The improvement in oxidation resistance which results from the addition of substantial quantities of zirconium⁴, chromium⁵, silicon⁶, aluminium⁷ and combinations of cobalt and iron, cobalt and nickel, chromium and cobalt or chromium and nickel⁷ is believed to be derived from the formation in the scale of oxides other than Nb_2O_5 . However, large additions of these elements have a detrimental effect on the ductility or refractoriness of niobium. For this reason, attention was concentrated upon small additions of those elements which exert their effect on oxidation resistance primarily by their influence on the Nb_2O_5 in which they dissolve.

One exception is the systematic improvement in oxidation resistance resulting from the addition of up to about 25 at. % titanium, which produces scales containing 3 $\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ beyond about 6 at. % titanium in the alloy⁸. In this case, however, the improvement is not only due to the formation of another phase, as a definite improvement occurs up to 5 at. % titanium and the influence of dissolved titanium on Nb_2O_5 must be significant.

The effect of alloy cation size on the dimensions of Nb_2O_5

In assessing the influence of the alloy cation size on the oxide: metal volume ratio, its effect on the dimensions of both the oxide and metal lattices must be considered. Further, since the metal cations occupy a minor part of the oxide volume, any variation in their dimensions has a proportionally reduced effect on the oxide dimensions. Although an added element will exert a different dimensional effect in the ionised state of the oxide to that in the metallic lattice, in general, the relative effects of the elements which have been studied are about the same in both environments. Because of these considerations, the oxide:metal volume ratio is hardly affected, unless the atomic radii of the constituent elements are markedly different and one of them is appreciably concentrated in the oxide.

KLOPP *et al.*⁹ found that, after exposure to air at 800°C, the concentrations of titanium, vanadium, tantalum, tungsten and zirconium in the scale and in the niobium alloy core differed by only 25% or less. Furthermore, the atomic radii differences are so small that it can be shown that the total effect on the oxide: metal volume ratio is insignificant.

The influence of addition valency on oxide stoichiometry and the dimensions of Nb₂O₅

The high oxide: metal volume ratio of Nb₂O₅ is due to the large volume of the oxide occupied by oxygen atoms. The addition of elements with lower effective valencies than that of niobium should therefore reduce the volume ratio and the tendency to cracking.

At 1,000°C, in those composition ranges where only niobium oxides are formed in the scale, the following observations are made:

(i) of the quadrivalent elements titanium, zirconium and silicon, titanium^{3,9,10} improves the oxidation resistance of pentavalent niobium, whilst zirconium^{4,9,10} and silicon⁶ reduce it;

(ii) vanadium, which can exhibit valencies of both 4 and 5, markedly improves the oxidation resistance^{7,9,10};

(iii) molybdenum, with alternative valencies both higher (6) and lower (4) than niobium, also improves the oxidation resistance^{7,9,10};

(iv) tungsten, with the same possible valencies as molybdenum, was initially reported to be detrimental^{9,10,11} but later investigations by MICHAEL⁷ have shown that it can have a beneficial effect at 1,100°C;

(v) chromium, with alternative valencies of 6 and 3, has also been found beneficial^{9,11}; There appears, therefore, to be no simple consistent relationship between the influence of an added element and its valency.

The influence of addition valency on oxygen diffusion in Nb₂O₅

Nb₂O₅ possesses an oxygen-deficient lattice^{12,3} and by virtue of the Wagner concept¹³ alloy cations having a *higher* valency than niobium should, on solid solution in Nb₂O₅, reduce the number of lattice defects and thus the diffusion rate of oxygen through the adherent compact scale. Elements of lower valency should have the opposite effect. The relevant experimental findings are therefore the same as those discussed in the preceding section, but the effects of valency in the two cases are diametrically opposed, and there is no consistent experimental support for either mechanism.

Relaxation of internal stresses within the adherent scale

It has been suggested by KLING³ that the creep strength of the Nb₂O₅ scale may be related to ionic mobility, and therefore to the anion deficiency, by analogy with the state of affairs in metals. Accordingly, if the controlling factor in the influence of added elements on oxidation is the ease of plastic deformation in the scale, the effects of valency are opposed to those which were considered in the preceding section.

However, our knowledge of the deformation processes in oxides is very limited, and it is probable that the influence of added elements is much more complex than

that suggested above. Perhaps both the foreign ions and the defect lattice sites together introduce internal stresses which help to increase the apparent creep-strength.

Fracture strength of the adherent scale

Our understanding of the factors influencing the fracture strength of oxides is also limited, and although it is probable that added elements will have an appreciable effect on this property, the form that this will take cannot easily be predicted. The possibility of valid experimental assessment of the influence of additions is made difficult by the need to use specimens which are in the same condition as the thin compact and adherent scale.

Healing of the outer porous scale by sintering

Although sintering of the outer porous scale may in some cases contribute towards a reduction in the rate of oxidation, it has been observed by previous workers and during the present investigation that the best alloys are characterised by a dark adherent underlying scale which is relatively thick compared with that on pure niobium. Further, during the present investigation it was found that the light-coloured outer oxide formed much later on the oxidation-resistant alloys than on niobium, but after a shorter period on alloys containing silicon and zirconium. These observations suggest that the increased protection afforded by beneficial elements is primarily associated with their influence on the underlying dark adherent scale.

There are other possible mechanisms of protection, in addition to the general ones discussed above, which may only operate in the case of a limited number of alloying elements. Thus, the beneficial effect produced by small percentages of molybdenum may be due to partial volatilisation of molybdenum as MoO_3 which is suggested by the analytical results of KLOPP *et al.*⁹. Such volatilisation at low molybdenum concentrations may reduce the oxide: metal volume ratio, while at higher molybdenum contents the more marked volatilisation would probably introducedeleterious porosity into the scale.

From the foregoing analysis of previous experimental work, it is clear that none of the proposed mechanisms is capable of explaining the effect of added elements on niobium oxidation in all cases, and the influence of each addition is probably due to a complexity of factors. There was, therefore, no theoretical lead as to the direction the present research should take in the development of ternary and more complex alloys having improved oxidation resistance. However, from the limited data^{10,14} which were available at the initiation of the project, the indications were that titanium was the most useful of the binary additions studied. Titanium had been shown to promote a substantial improvement in oxidation resistance up to temperatures of at least $1,100^\circ\text{C}$, and also to reduce the embrittlement produced by interstitial contaminants and certain alloying elements in substitutional solid solution, without much effect on the refractoriness of niobium. Accordingly, this investigation was principally concerned with examining systematically the effects of further additions to niobium-titanium alloys.

EXPERIMENTAL PROCEDURE

Scope of research

The investigation began with a general survey of the effects of a wide range of

elements, including Mo, W, Ta, V, Zr, Cr, Fe, Ni, Co, Mn, B, Re, Ce, Al and Si, on the oxidation resistance of niobium containing 9, 18 or 25 at. % titanium. A simple gravimetric test was used. From the results of the preliminary survey a number of alloys were selected for more complete investigation by means of a continuously indicating spring balance.

Intensive oxidation-testing was then carried out in certain promising alloy ranges, in order to determine the optimum compositions and to assess the influence of temperature and of still further added elements.

The entire investigation was supported by X-ray and chemical analysis of the samples, and by metallographic examination and micro-hardness testing of the metal used.

Experimental methods

The materials used in preparing alloys were as follows:

Niobium: Murex Ltd., Powder, minus 20 mesh (0.30% Ta, 0.03 Fe, less than 0.01% C, 0.01% N, 0.01% Pb, 0.01% Sn, 0.01% Si and 0.03% Ti)

Titanium: I.C.I. Ltd., sponge (evaluation hardness 135–145 V.P.H.)

Zirconium: Murex Ltd., sponge (evaluation hardness 140–150 V.P.H.)

Other constituents: Ta, V, W, Mo, Fe, Ni, Co and Cr. Johnson Matthey & Co Ltd., spectrographically pure (99.99%)

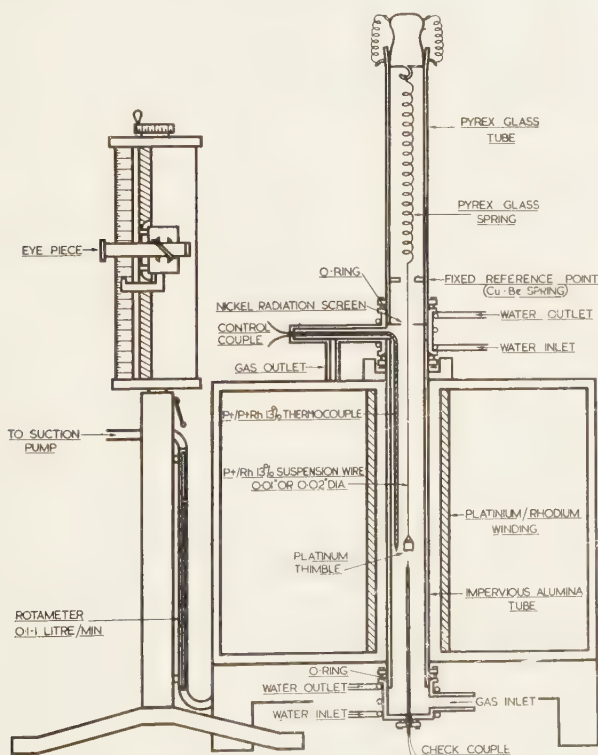


Fig. 1. Spring balance for high-temperature oxidation-testing.

The alloys were melted in a tungsten-electrode arc furnace containing an atmosphere of purified argon, after evacuation of the furnace chamber to $2 \cdot 10^{-2}$ mm Hg.

The preliminary survey was mainly conducted upon small specimens, approximately 4 mm cube and weighing about 1 g, machined from 5 g alloy buttons and the faces ground, polished on fine emery paper and degreased. A number of long-term tests were conducted on 2 g rectangular specimens and these are identified later. The specimens were placed in an alumina boat, introduced into a tube furnace open to the atmosphere, and the original dimensions and increase in weight after exposure used to calculate the degree of oxidation in terms of weight increase per unit area. In order to cover an extensive composition range a standard comparative test of 1 h at $1,100^{\circ}\text{C}$ was adopted for nearly all the alloys, but additional treatments of varied duration at $1,100^{\circ}\text{C}$ and other temperatures have also been applied to individual alloys.

Information on the progress of oxidation in certain selected alloys was obtained by testing in the apparatus illustrated in Fig. 1, using undried air flowing at a rate of 0.5 l/min. Specimens about 3 mm square and 1 mm thick, weighing about 0.4 g were placed in a small platinum thimble, which was suspended by a platinum/13% rhodium wire in a vertical tube furnace from a calibrated Pyrex glass spring. The deflection of the spring, which measured the weight of the wire, thimble and contents, was followed by means of a travelling microscope. The static gravimetric test in a modified form was reverted to in the final series of tests, since its simplicity enabled the examination of a wider range of alloy compositions in a given time.

During the preliminary survey small rectangular test specimens were used, but these were susceptible to the considerably accelerated oxidation noted at edges and

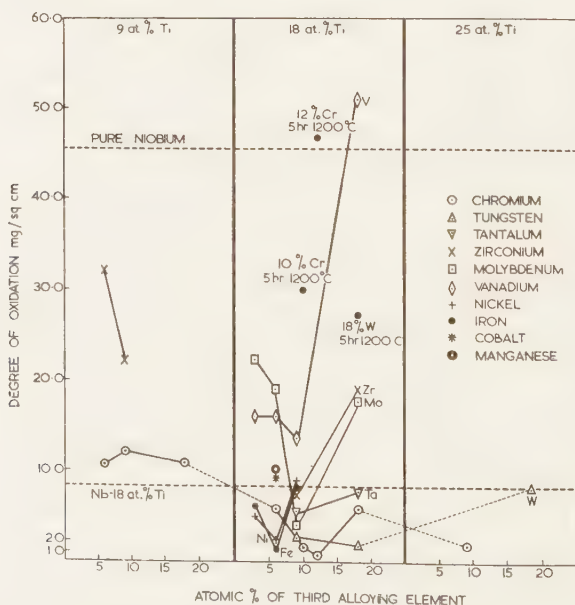


Fig. 2. Degree of oxidation in air of ternary niobium alloys containing 9, 18 or 25 at. % titanium, after 1 h at $1,100^{\circ}\text{C}$ (1 g rectangular specimens).

sharp projections on niobium alloys. This irregular surface oxidation was considered undesirable and was largely avoided in the second extensive survey, by carrying out the tests on approximately spherical 1 g specimens. A standard comparative test of 1 h at 1,100°C was established for all alloys, but a considerable amount of testing was carried out at other temperatures and also for periods of 1, 2, 40, 50 and 100 hours. As oxidation proceeds the surface area of the unoxidised metal decreases and therefore the oxidation data reported in the first survey, which was calculated on original area, is too low. In the second survey, using spherical specimens, the mean of the original and final surface area was used to calculate an oxidation rate which is a closer approximation to the true one.

EXPERIMENTAL RESULTS

Preliminary survey on the effect of additions to niobium-titanium alloys

The results of oxidation tests on rectangular ternary niobium-alloy specimens containing 9, 18 or 25 at. % titanium are given in Table I. The results of the 1-h tests at 1,100°C and certain other tests are also presented graphically in Fig. 2.

TABLE I

DEGREE OF OXIDATION OF TERNARY NIOBIUM ALLOYS

(Total weight gain in mg/cm² on 1 g and 2* g rectangular specimens)

Nominal alloy composition (atomic %)	Time and temperature of exposure			
	1 h/ 1,100°C	5 h/ 1,100°C	100 h/ 1,100°C	1,200°C
Pure niobium	45.8			
Nb - 18 Ti	7.7			
- 18 Ti - 3 Mo	22.0			
- 18 Ti - 6 Mo	19.0			
- 18 Ti - 9 Mo	4.2	63.2		
- 18 Ti - 18 Mo	18.0			
- 18 Ti - 9 W	3.3	11.0	244.9*	
- 18 Ti - 18 W	2.0	16.8		27.0 (5 h)
- 25 Ti - 18 W	8.1			
- 18 Ti - 12 W			149.0*	
- 18 Ti - 9 Ta	5.0			
- 18 Ti - 18 Ta	7.4	29.2		
- 18 Ti - 3 V	17.0			
- 18 Ti - 6 V	16.8			
- 18 Ti - 9 V	14.0			
- 18 Ti - 18 V	52.0	c.o.		c.o. (5 h)
- 9 Ti - 6 Cr	10.8			
- 9 Ti - 9 Cr	12.0			
- 9 Ti - 18 Cr	11.0			
- 18 Ti - 6 Cr	5.8			123.0 (25 h)
- 18 Ti - 10 Cr	1.4	7.0		29.9 (5 h)
- 18 Ti - 12 Cr	0.7			47.2 (5 h)
- 18 Ti - 18 Cr	6.0			
- 25 Ti - 9 Cr	2.0		270.2*	c.o. (18 h)
- 9 Ti - 6 Zr	32.0			
- 9 Ti - 9 Zr	22.0	c.o.		
- 18 Ti - 6 Zr				101.8 (5 h)
- 18 Ti - 9 Zr	7.0	31.0		
- 18 Ti - 18 Zr	19.0			

TABLE I (continued)

Nominal alloy composition (atomic %)	Time and temperature of exposure			
	1 h/ 1,100°C	5 h/ 1,100°C	100 h/ 1,100°C	1,200°C
- 18 Ti - 3 Ni	5.5	17.6		
- 18 Ti - 6 Ni	1.8			
- 18 Ti - 9 Ni	8.5	22.5		
- 18 Ti - 3 Fe	6.0			
- 18 Ti - 6 Fe	9.6 0.75 2.3	} Mean 1.22		c.o. (25 h)
- 18 Ti - 9 Fe	8.4 7.7			
- 18 Ti - 6 Co	9.0			
- 18 Ti - 6 Mn	10.0			

2 g specimens denoted by *

c.o. = complete oxidation.

Certain ternary alloys containing Cr, Fe, Ni, Mo, W or Ta were found to be superior to niobium-18 at. % titanium and on the basis of the one hour tests at 1,100°C it appeared that controlled additions of tungsten, nickel, iron and chromium might reduce the oxidation rate to less than 10% of that of niobium. The limited number of tests which were carried out at 1,200°C and for longer times at 1,100°C generally confirmed these findings.

TABLE II

DEGREE OF OXIDATION OF TERNARY AND QUATERNARY ALLOYS
(Total weight gain in mg/cm² on 2 g and 1 g* rectangular specimens)

Nominal alloy composition (atomic %)	Time and temperature of exposure			
	1 h/ 1,100°C	20 h/ 1,100°C	100 h/ 1,100°C	16 h/ 1,180°C
Nb - 18 Ti	13.1		320 (M)	
- 25 Ti - 9 W	4.7			98.9
- 22 Ti - 9 W	3.0			79.3
- 22 Ti - 18 W	12.1			148.7
- 18 Ti - 9 W - 3 Cr	1.4*			
- 18 Ti - 9 W - 6 Cr	1.5*			
- 25 Ti - 9 W - 6 Cr	16.4		321.6(M)	
- 18 Ti - 10 Cr - 2 Ce	16.2		281.9(M)	
- 30 Ti - 12 Cr	22.1			
- 18 Ti - 9 W - 6 Ni	0.8*			
- 18 Ti - 9 W - 3 Ni			161.8(M)	
- 18 Ti - 9 W - 3 V	15.0	c.o.		
- 18 Ti - 9 W - 6 V	15.3	219.7		
- 18 Ti - 9 W - 3 Ta	11.2	66.6		
- 18 Ti - 9 W - 6 Ta	17.5	113.7		
- 18 Ti - 6 Ce	c.o.*			
- 18 Ti - 6 Al	6.6*			
- 18 Ti - 6 Si	13.6*			
- 18 Ti - 6 Re	8.0*			
- 18 Ti - 1 B	18.5*			
- 18 Ti - 2 B	21.0			
- 18 Ti - 15 W - 2 Ce	14.6		213.8(M)	
- 33 Ti - 33 Cr	0.6*			20 (20 h)*
- 50 Ti - 10 Zr	23.0*			

1 g specimens denoted by *.

(M) = The mean of the original and final surface areas used.

c.o. = complete oxidation.

Tests were next conducted on some other ternary alloys and niobium-titanium-tungsten alloys containing quaternary additions of nickel, chromium, vanadium and tantalum. The results, presented in Table II, indicated that nickel and chromium additions improved the oxidation resistance of niobium-18 at. % titanium-9 at. % tungsten but that vanadium and tantalum additions were detrimental.

These tests also suggested that higher percentages of titanium would not lead to marked improvement in oxidation resistance. Also, titanium, together with iron, nickel and chromium, was expected to decrease, and tungsten to increase, the rectoriness. This was confirmed during a programme of high-temperature creep-testing, subsequently carried out on a wide range of niobium alloys. It was therefore decided generally to adopt a titanium level of 20 at. % in later tests as a compromise between the requirements of oxidation resistance and ductility on the one hand and strength on the other.

Additional specimens were also prepared from each alloy in Tables I and II, for workability assessment, conducted at room temperature. Most of the alloys with the notable exception of those containing chromium, were quite ductile and many withstood 60% deformation by pressing, with only slight edge cracking. The addition of 2 at. % cerium to niobium-18 at. % titanium-10 at. % chromium was found not to improve the ductility significantly. Although chromium was established to be a beneficial addition, the presence of titanium did not sufficiently reduce its embrittling effect: and thus chromium was rejected as a basic ternary addition for immediate study.

Oxidation testing of selected alloys by means of the thermal spring balance

The results of the preliminary survey, which indicated the beneficial effect of W, Ti, Fe and Cr additions, were derived from a limited number of tests of fixed duration and did not elucidate the mode of oxidation. Accordingly, a limited number of alloys were selected for examination on the spring balance and some oxidation curves typical of those obtained are presented in Fig. 3. It was found in all cases that the oxidation

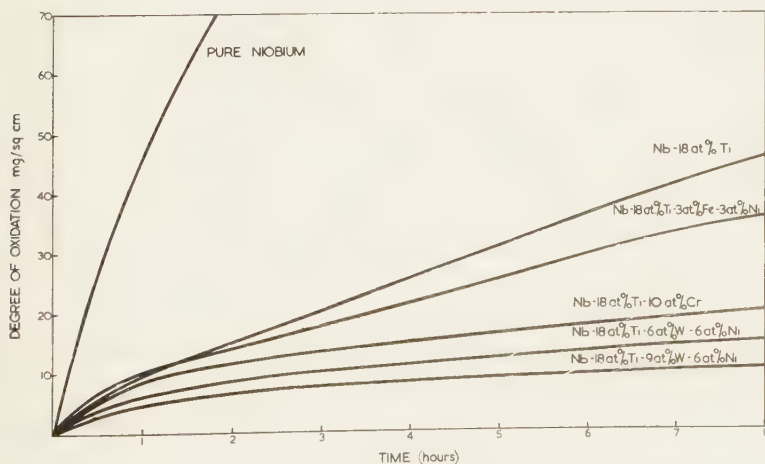


Fig. 3. Oxidation of some niobium alloys in air at 1,100°C. Weight increase continuously recorded by Pyrex spring balance.

decreased in a parabolic fashion during the first one or two hours, after which the specimen oxidised in an approximately linear manner during the next few hours. After a period of exposure dependent on the size and oxidation resistance of the specimen, the oxidation rate, calculated on the original surface area, deviated progressively from linearity as the effective surface area of the residual metal core decreased. It was concluded that with the size and type of specimen and form of apparatus used the oxidation rate could only be recorded reliably on tests of up to about 8 hours. For this reason the curves presented are only for 8 hours although three of the specimens were tested for over 45 hours. Tests of over 200 hours have been conducted on Nb-18 at. % Ti-9 at. % W, -6 at. % Ni; Nb-18 at. % Ti-9 at. % W-3 at. % Ni; and Nb-18 at. % Ti-15 at. % W; which confirmed the regular nature of the oxidation process for these alloys during the longer exposure periods, although the later oxidation rates had no absolute significance due to the consumption of much of the specimen.

The tests carried out on the spring balance confirmed that the alloy combinations selected during the preliminary survey had considerable oxidation resistance relative to niobium and that they appeared to remain effective for long periods (up to 300 h) and over the temperature range $1,000^{\circ}$ - $1,200^{\circ}\text{C}$.

At this stage it was decided to determine the optimum alloy compositions more precisely and to assess the inter-related effect of the beneficial added elements.

Influence on oxidation-resistance of small variations in the level of tungsten, nickel, iron and cobalt additions

Variation of tungsten in 20 at. % titanium alloys (Fig. 4). The results from tests

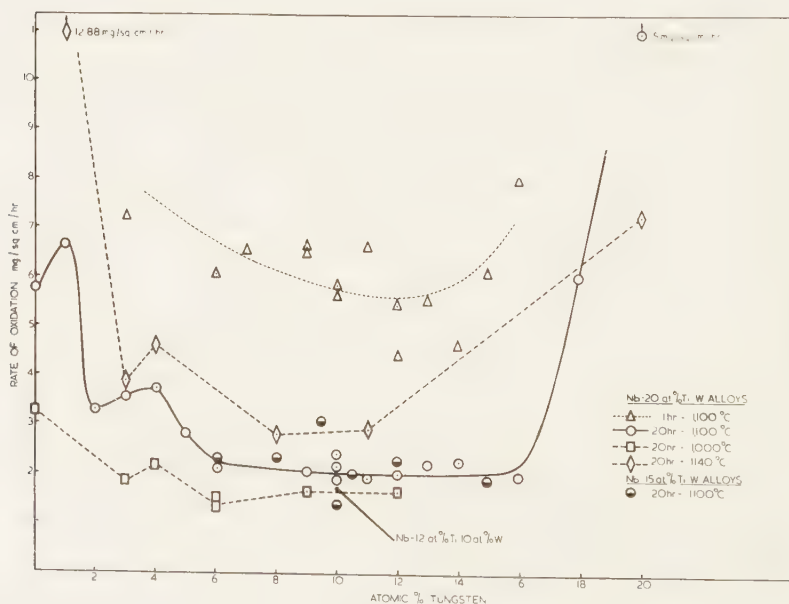


Fig. 4. Oxidation rates of niobium-20 at. % titanium-tungsten alloys in air at $1,000^{\circ}\text{C}$, $1,100^{\circ}\text{C}$ and $1,140^{\circ}\text{C}$.

conducted at 1,000°, 1,100° and 1,140°C all indicated that the influence of tungsten additions up to about 4 at. % is complex. There is evidence of an initial decrease in oxidation resistance at 1 at. % tungsten followed by a general but fluctuating improvement up to 6 at. % tungsten. Further additions of tungsten up to about 16 at. % do not produce any significant variation in oxidation resistance at 1,100°C, but larger additions result in a pronounced deterioration.

The rate of oxidation of Nb-20 at. % Ti-20 at. % W at 1,100°C was greater than that at 1,140°C; but generally, the effect of tungsten follows the same trend at 1,000°, 1,100° and 1,140°C, with a progressive increase in the oxidation rate with temperature. It was noted that the beneficial effect of tungsten additions was less pronounced at 1,000°C than at 1,100°C. Oxidation rates determined from 1-h tests at 1,200°C were found to be 2 to 3 times greater than those at 1,100°C.

Reduction in the titanium content from 20 at. % to 15 at. % did not have any significant effect on the oxidation resistance of niobium alloys containing from 6 to 15 at. % tungsten.

A wide range of tungsten additions therefore double the oxidation resistance of niobium-20 at. % titanium but as the tungsten content is increased the ductility gradually deteriorates and the practical limit is probably about 12 at. %.

Variation of nickel, iron and cobalt in 20 at. % titanium alloys (Fig. 5). The addition of up to 8 at. % nickel leads to a progressive increase in the oxidation resistance of niobium-20 at. % Ti alloys, and an increase in the titanium level to 25 at. % only produced a significant improvement in the case of the 5 at. % nickel alloy.

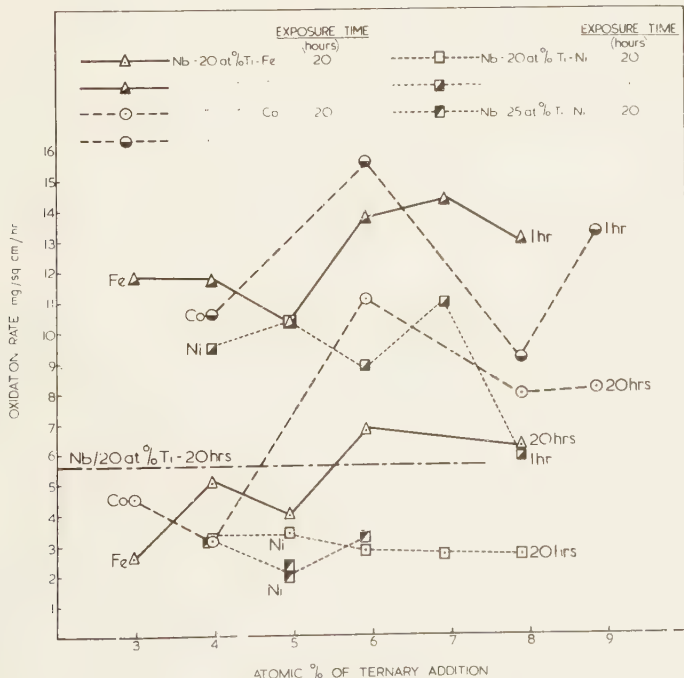


Fig. 5. Oxidation rates in air at 1,100°C of Nb-20 at. % Ti or Nb-25 at. % Ti alloys containing ternary additions of iron, nickel or cobalt.

Iron appears to differ from nickel in that only small additions produce an improvement in oxidation resistance; and 20 at. % titanium alloys containing 6 and 8 at. % iron are inferior to the iron-free alloy. The 1-h oxidation rates are also noticeably high. Similarly, only small additions of cobalt (3 and 4 at. %) were found beneficial and larger additions drastically reduced oxidation resistance.

Variation of nickel in titanium-tungsten alloys (Fig. 6). At 1,100°C, a significant decrease in oxidation resistance was observed on the addition of 1 at. % nickel to niobium-20 at. % titanium-10 at. % tungsten; but further additions of 2 and 3 at. % nickel lead to a progressive improvement. Alloys containing between 3 and 7 at. % nickel showed some scatter, but the oxidation resistance remained approximately constant.

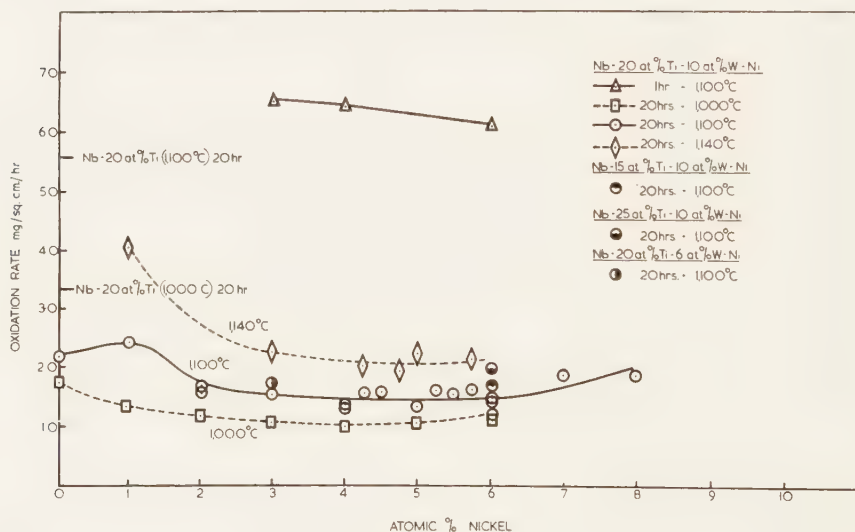


Fig. 6. Oxidation rates of niobium-titanium-tungsten-nickel alloys in air at 1,000°C, 1,100°C and 1,140°C.

The effects of increasing nickel contents at 1,140°C and 1,100°C are similar, with 1 at. % nickel probably having a detrimental effect; but at 1,000°C, a progressive improvement was recorded up to 4 at. % nickel. It appears that, on increasing the temperature from 1,000° to 1,140°C, the oxidation rate of niobium-20 at. % titanium-10 at. % tungsten-1 at. % nickel increases more rapidly than that of alloys containing larger nickel additions, so that only the higher contents are beneficial at the higher temperatures.

Increasing the titanium content of the 10 at. % tungsten-6 at. % nickel alloy to 25 at. % resulted in an appreciable decrease in oxidation resistance, whilst the effect of a decrease to 15 at. % was insignificant. The effect of a reduction in the tungsten content of the niobium-20 at. % titanium-10 at. % tungsten-3 at. % nickel alloy to 6 at. % tungsten was also insignificant.

Variation of cobalt in titanium-tungsten alloys (Fig. 7). The effects of cobalt on niobium-20 at. % titanium-10 at. % tungsten and niobium-20 at. % titanium are

similar, in that additions of 2, 3 and 4 at. % cobalt slightly improve the oxidation resistance, whilst 6 and 8 at. % cobalt markedly reduce it.

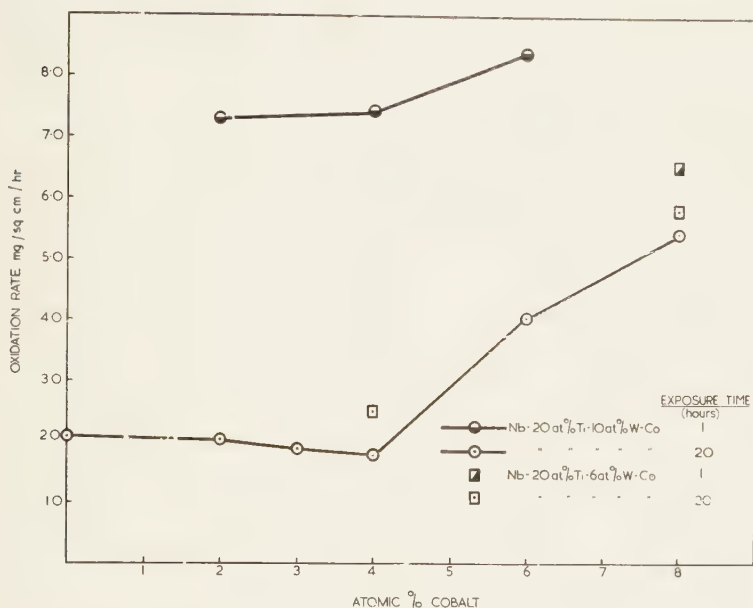


Fig. 7. Oxidation rates of niobium-20 at. % titanium-tungsten-cobalt alloys in air at 1,100°C.

Metallographic and X-ray examinations

A representative programme of metallographic and X-ray examinations was conducted simultaneously with the oxidation testing, but this did little to elucidate the mechanism of protection by alloying. Generally two layers of oxide-scale, porous and compact, were observed; together with a hardened and differentially-etching metallic surface zone. The more oxidation-resistant alloys were found to possess a thicker underlying layer of dark scale.

The additions of tungsten, nickel, molybdenum, iron, chromium and cobalt examined produced only slight modifications to the $3 \text{ Nb}_2\text{O}_5 \cdot \text{TiO}_2$ scale formed on niobium-20 at. % titanium but the effects of other elements were more complex.

DISCUSSION OF RESULTS

Review of findings

The outcome of the investigation was that niobium alloys containing 15-25 at. % titanium and 6-10 at. % tungsten provided the most promising base for the development of high-temperature high-strength alloys, since the oxidation resistance was superior to the other ductile alloys studied, and subsequent testing had shown that their creep strength was of the same order as that of niobium.

Nickel was found to be an effective beneficial addition to the niobium-titanium-tungsten base and an alloy of niobium-20 at. % titanium-10 at. % tungsten-4 at. %

nickel had the maximum oxidation resistance over the temperature range from 1,000° to 1,140°C. A reduction in the tungsten content to 6 at. % improves the ductility without any significant effect on oxidation resistance, but the creep-strength is reduced. On the other hand, a reduction in the nickel content to 2 at. % improves to some extent the ductility and creep-strength but reduces the oxidation resistance. Other modifications of the more promising compositions were examined (Table III), but no further significant improvement was noted.

TABLE III
OXIDATION RATE OF SOME COMPLEX NIOBIUM ALLOYS
(Weight gained in mg/cm²/h on 1 g spherical specimens)

Nominal alloy composition (atomic %)	Time and temperature of exposure		
	20 h/ 1,000°C	20 h/ 1,100°C	20 h/ 1,140°C
Nb - 20 Ti - 6 W	1.5		
- 20 Ti - 6 W - 1 Zr	2.4		
- 20 Ti - 8 W			2.8
- 20 Ti - 6 W - 3 Cr			3.3
- 20 Ti - 6 W - 4 Co			4.6
- 20 Ti - 6 W - 4 Co - 3 Cr			3.1
- 20 Ti - 10 W		2.0	
- 20 Ti - 10 W - 1 Zr		4.4	
		2.8	
- 20 Ti - 10 W - 4 Ni		1.4	
- 20 Ti - 10 W - 4 Ni - 5 Al		1.7	
- 20 Ti - 10 W - 3 Ni - 3 Cr			11.8
- 20 Ti - 10 W - 3 Ni - 2 Cu		1.6	
- 20 Ti - 10 W - 3 Ni - 2 Mn		1.9	

Spherical 1 g specimens used, and oxidation rate calculated from the mean of original and final surface area.

A more practical indication of the potential of the oxidation-resistant alloys was obtained from a number of 100 h oxidation tests which were conducted. For example, on exposure at 1,100°C, approximately 1 g spherical specimens of unalloyed niobium and niobium-20 at. % titanium-10 at. % tungsten-2 at. % nickel oxidised by 97 mg/cm² in 1 hour and 70 mg/cm² in 100 h, respectively, indicating more than a hundredfold increase in oxidation resistance.

This order of improvement is inadequate for most applications involving oxidising atmospheres above 1,000°C; but if a satisfactory protective coating could be applied, the refractory oxidation-resistant alloys could be used for the component core, thus reducing the seriousness of any localised coating failure. Further, the range of possible additions to the niobium titanium tungsten and niobium titanium-tungsten-nickel alloys has by no means been exhausted, and some new addition or a variation in the relative levels of additions already examined will possibly lead to some further improvement in oxidation resistance without a marked deterioration in other desirable properties.

Mechanism of protection

Since tungsten, nickel, iron and cobalt additions introduced no additional oxides

to the scale on niobium-20 at. % titanium alloys their beneficial effect probably derives from their influence on $3\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ by minor solid solution.

No structure determination of $3\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ is available; but it is clear from the X-ray diffraction pattern that the structures of $\beta\text{Nb}_2\text{O}_5$ and $3\text{Nb}_2\text{O}_5 \cdot \text{TiO}_2$ are closely allied. However, additional elements do not always influence the protective qualities of the two oxides in the same way. For example, 9 at. % zirconium was found to have a slightly beneficial effect on niobium-18 at. % titanium compared with its established detrimental effect on niobium itself, while 9 at. % vanadium had a detrimental effect compared with its known beneficial effect on pure niobium.

The inter-related effects of the principal beneficial elements on the performance of the niobium-20 at. % titanium base can be assessed from Figs. 4 to 7. The effect of cobalt variations in the niobium-20 at. % titanium-10 at. % tungsten-cobalt alloys is similar to that observed for niobium-20 at. % titanium-cobalt alloys, with a rapid decrease in oxidation resistance at 6 and 8 at. % cobalt. On the other hand, in the niobium-20 at. % titanium-10 at. % tungsten-nickel alloys a high level of oxidation resistance is maintained throughout the range 4-8 at. % nickel, as in the niobium-20 at. % titanium-nickel alloys. Furthermore, a variation in the tungsten content of both the niobium-20 at. % titanium and niobium-20 at. % titanium-3 at. % nickel alloys from 6 to 10 at. % tungsten produces no significant effect on the oxidation resistance. Since the effects of nickel and cobalt are additive to, and probably unrelated to, that of tungsten, it is possible that the mechanisms by which they produce a protective scale are different.

CONCLUSIONS

A decrease in the oxidation of niobium by a factor of one hundred has been accomplished by alloying with about 20 at. % titanium, 10 at. % tungsten and 3-4 at. % nickel.

Modification of the above composition within the limits 15-25 at. % titanium, 0-14 at. % tungsten, 0-4 at. % nickel produces other levels of ductility and creep strength which are suitable for many applications, but some reduction in oxidation resistance also occurs.

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DEVELOPMENT OF OXIDATION RESISTANCE OF
SOME REFRACTORY METALS

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SUMMARY

Investigations into the protection of niobium and molybdenum from oxidation by alloying and by applied coatings are described. The niobium alloy containing 17.5 at. %* tungsten, 17.5 at. % titanium and 5 at. % iron shows a great improvement in oxidation resistance over unalloyed niobium, but is not to the standard required for an oxidation-resistant alloy. An aluminium-chromium-silicon coating affords protection to molybdenum against oxidation at 1,200°C for 150–200 hours and the coating shows considerable resistance to thermal shock. Attempts to apply a protective coating to niobium have not been successful.

INTRODUCTION

Some refractory metals which have the most promising properties for high temperature applications are tungsten, molybdenum, tantalum and niobium, despite the fact that they are characterised by a high rate of oxidation in air. Some method of protection is therefore necessary if these metals are to be employed for high temperature purposes. In general there are two methods of protection from oxidation applicable to these metals: either the metal can be protected by alloying with another metal so that the oxide film produced is protective, or a coating can be applied to the metal which will prevent or restrict access of oxygen to the base metal. In either case the protection must be carried out in such a way as to retain the desirable high temperature characteristics of the metal — strength at temperature, resistance to impact and resistance to thermal shock.

The object of the work described in this paper was to see whether the oxidation resistance of the two metals molybdenum and niobium could be increased by alloying or by coating so that their use in gas turbine engines and other high temperature applications might be considered further. Since the Nimonic alloys were already capable of operating at temperatures of approximately 900°C, protection was sought for a minimum temperature of 1,000°C and preferably 1,200°C. The rate of oxidation of Nimonic 95 at 950°C was taken as the criterion by which the oxidation behaviour of alloys or coatings (at any temperature) would be judged, Nimonic 95 being considered to have adequate, but only just adequate, resistance to oxidation at this temperature.

Abbreviations: % = weight %; at. % = atomic %.

NIOBIUM ALLOYS

It was felt at the outset of this particular investigation that oxidation resistance was the first objective and somewhat loose limits were set on parameters such as adequate strength at the maximum working temperature and adequate ductility to permit mechanical working at either room or elevated temperatures. A lower limit of 1,800°C was set on melting point on the grounds that any lower melting alloy was unlikely to have sufficient strength without a prolonged heat treatment study. Ductility tests have been somewhat crude, hand hammer forging tests on the as-cast or homogenised buttons having been used to determine whether or not any deformation occurred before fracture.

Alloys were prepared by arc melting 50 g pellets pressed from a mixture of sheet clippings or powders of the addition metals with coarse (—20 + 60 mesh) granules of niobium. Care was taken to maintain a low concentration of interstitial elements in the arc-melted buttons because of their pronounced effect on the ductility of niobium. The source and purity of materials used in this work are given in Table I.

TABLE I
PURITY OF MATERIALS EMPLOYED

Metal	Source	Analysis %							
		O	C	N	H	Fe	Si	Ti	Miscellaneous
Niobium	Murex	~0.03	0.01	0.03	<0.005	0.03	0.01	0.01	0.3 Ta
Tantalum	Murex	0.01	0.02	0.02	<0.005	0.02	0.01	0.01	0.1 Nb
Silicon	Sweden	—	—	—	—	0.5	99.0	—	0.25 Ca
Zirconium	Murex	0.1	0.01	0.01	<0.01	0.03	—	0.01	2% HF
Chromium	Murex	—	0.015	—	—	trace	trace	—	Electrolytic flake
Molybdenum	Murex	0.05	0.005	—	—	0.005	0.02	—	
Tungsten	Murex	—	—	—	—	0.005	—	—	0.05 Mo
Vanadium	Magnesium Electron Ltd.	0.12	0.05	0.05	0.05	0.3	0.1	—	0.25 Mg; 0.1 Cl
Zinc	Hopkin and Williams	—	—	—	—	0.002	—	—	
Manganese	Murex	—	0.03	—	—	0.8	0.5	—	1.59 Al
Titanium	I.C.I.	Commercially pure arc-melted stock							
Aluminium	B.A.C.O.	Pure Notch bar 99.9 + Al							
Iron	G. Cohen Ltd.	Electrolytic powder 99.4–99.8 – re-reduced in hydrogen							
Cobalt	Murex	Hydrogen-reduced powder 97.6–98%. Co re-reduced before use							
Nickel	Mond Nickel Co.	Carbonyl powder 99.3–99.7% re-reduced in H ₂							
Rare earths		Produced as Mischmetall 45–55% Ce, 25% La remainder mainly Nd							

Melting was conducted in a low pressure (4 cm Hg) of gettered argon (Saturn Black Label Grade 99.9% +) on a water-cooled copper hearth using a non-consumable tungsten electrode. The leak rate of the furnace was checked before each melt and maintained at less than 0.5 μ l/sec. Each pellet was arc-melted at least three times, turning the button between melts to obtain a button free from segregation. Where a promising composition was obtained, a further homogenising heat treatment for a

prolonged period at high temperature (for example 20 h at $1,700^{\circ}\text{C}$) was given. Specimens $0.5\text{--}0.6\text{ cm square} \times 1\text{--}1.5\text{ cm long}$ were cut from these buttons.

Oxidation tests were carried out in a tube furnace using a 2 in. internal diameter impervious mullite tube, the closed end of which was inserted into a recrystallised alumina high temperature tube furnace wound with molybdenum and with a protective atmosphere of hydrogen. The furnace was controlled by a platinum rhodium thermocouple inserted into the annular space between the mullite and alumina tubes and temperature checks were made with an optical pyrometer. The specimens were supported during test on alumina tiles. Oxidation rate was determined by weighing the specimens before and after a given oxidation period — one hour, three hours or more depending on the resistance of the particular sample — and computing the gain in weight per/h/cm² of initial surface area of the specimen. Air saturated with water vapour at 18°C was passed down a narrow bore tube to the far end of the closed mullite tube at a rate of 4 l/min, giving a linear rate of 8 ft./min over the specimens — an excess of oxygen by a factor of $\times 60$ for that required to oxidise a typical charge completely in one hour.

Tests had shown that the presence of water vapour made little difference to the results of oxidation tests when considered in relation to the general level of the results. For instance, with unalloyed niobium at $1,200^{\circ}\text{C}$ an oxidation rate of $153\text{ mg/cm}^2/\text{h}$ was obtained for air dried over magnesium perchlorate, $168\text{ mg/cm}^2/\text{h}$ for air saturated with water at 18°C and atmospheric pressure and $202\text{ mg/cm}^2/\text{h}$ for air saturated at 45°C . Similarly the flow rate used was shown to be adequate. Oxygen was not used since air was considered to be more realistic with regard to possible applications.

Preliminary oxidation studies on binary alloy systems of niobium at $1,000^{\circ}\text{C}$ showed alloys with titanium, aluminium and chromium to be the most promising. Titanium was of particular interest since the alloy retained the ductility of the pure metals. Fig. 1 shows the effect of concentration of titanium on the oxidation resistance of niobium in air at $1,000^{\circ}\text{C}$. The results of the addition of vanadium to niobium were of interest (shown also in Fig. 1) in that the oxidation rate was reduced progressively to a total addition of about 10%, but then increased rapidly at 15–20% addition. The results of one hour tests on the most interesting binary alloys at $1,000^{\circ}\text{C}$ are shown in Table II. In view of results later obtained at $1,200^{\circ}\text{C}$ it is interesting to note that the addition of tungsten to niobium is detrimental to its oxidation resistance at $1,000^{\circ}\text{C}$. This result is confirmed by SIMS, KLOPP AND JAFFEE¹. Many other binary additions to niobium have been investigated including boron, zirconium, cadmium, silver, magnesium, copper and manganese, but in no case was there any real improvement in oxidation resistance.

At this stage in the work, ternary alloys based on the titanium, aluminium and chromium binary alloys were investigated and two alloys showed considerable promise, a niobium–aluminium–chromium (60:20:20 at. %) and niobium–aluminium–titanium (60:20:20 at. %) giving an oxidation rate at $1,000^{\circ}\text{C}$ of 2.95 and 2.1 mg/cm²/h respectively. Further additions to these alloys were made, and cobalt particularly was beneficial, reducing the oxidation rate at $1,000^{\circ}\text{C}$ of the niobium–aluminium–chromium alloy to 1.6 mg/cm²/h for the 60:17.5:17.5:5 at. % niobium–aluminium–chromium–cobalt alloy. However, further development along these lines was abandoned, since the alloys were brittle and had melting points as low as $1,400^{\circ}\text{C}$. It was therefore decided to concentrate on alloys with the refractory metals — with only

TABLE II
NOMINAL COMPOSITION AND OXIDATION TEST DATA FOR BINARY NIOBIUM ALLOYS

Alloy No.	Element addition	Nominal composition		Loss in weight/unit surface area after 1 h at 1000°C in air (mg/cm ²)	
		Atomic %	Weight %		
13/1	Unalloyed niobium	100	100	98,	95
13/2		—	—	118,	93
13/3		—	—	94,	96,
16/9		—	—	92,	91
					117
23/1	Beryllium	1	0.10	73,	78
23/2		5	0.51	89,	100
23/3		20	2.4	114,	92
24/4		40	6.1	16,	21
63/1	Aluminium	1	0.29	63,	74
63/2		5	1.5	96,	105
63/3		20	6.8	9.2,	9.2
7/1	Titanium	1	0.52	71,	72
7/2		5	2.6	80,	64
7/3		20	11.4	25,	18
3/1	Zirconium	1	0.98	120,	116
3/2		5	4.9	173,	156
3/3		20	19.7	59,	64
11/1	Silicon	1	0.30	187,	214
11/2		5	1.6	284,	285
11/3		20	7.0	115	
17/1	Tantalum	1	1.9	98,	105
17/2		5	9.3	102,	107
17/3		20	32.7	103,	105
19/1	Chromium	1	0.56	60,	73
19/2		5	2.9	74,	69
19/3		20	12.3	47,	56
18/1	Molybdenum	1	1.0	60,	59
18/2		5	5.2	32,	22
18/3		20	20.5	103,	157
21/1	Tungsten	1	2.0	150,	158
21/2		5	9.4	131,	115
21/3		20	33.1	169,	177
12/1	Iron	1	0.6	83,	76
12/2		5	3.1	78,	72
12/3		20	13.1	80,	76
8/1	Cobalt	1	0.64	96,	90
8/2		5	3.2	105,	124
27/1		20	13.7	64,	68
9/1	Nickel	1	0.61	92,	100
9/2		5	3.1	98,	113
9/3		20	13.2	56,	46
20/1	Rare earth elements added as Mischmetall	—	1	89,	96
20/2		—	5	167,	123
20/3		—	20	433,	346

minor additions of other metals — in order that the melting points should be kept high.



Fig. 1. Oxidation resistance of niobium and niobium/vanadium alloys at 1,000°C. — Niobium-titanium; — — — niobium-vanadium.



Fig. 2. Oxidation resistance of binary niobium alloys at 1,200°C. — Niobium-tungsten; — — — niobium-tantalum; — — — niobium-molybdenum; — — — niobium-zirconium; — — — — niobium-titanium.

Simultaneously with this, it was decided to test at a higher temperature, namely 1,200°C, and various binary alloys were retested at this temperature. The rate of oxidation at this temperature for niobium-tungsten, niobium-tantalum, niobium-molybdenum, niobium-zirconium, niobium-titanium, binary alloys plotted against composition is shown in Fig. 2. Several points of interest arise from these alloy systems. Addition of tungsten to niobium effects an immediate and marked improvement in the oxidation rate in contradiction to the results obtained at 1,000°C. Tantalum increases the oxidation rate in concentrations up to 20 at. % but further addition causes a rapid increase. Molybdenum and zirconium show a similar effect. Titanium and tungsten both reduce the oxidation rate and form a natural choice for further binary alloys. In fact the substitution of niobium by 20 at. % titanium in the 80:20 niobium-tungsten alloy — the most promising niobium-tungsten alloy — reduced the rate of oxidation from 26 mg/cm²/h to about 11 mg/cm²/h. Table III shows results of variations on this composition and indicates that best results are obtained with a minimum of 20 at. % of both tungsten and titanium.

Additions of molybdenum, vanadium, tantalum and zirconium to the niobium-tungsten binary system were investigated, but all appeared to be detrimental

TABLE III

COMPOSITION AND OXIDATION RATES IN AIR AT 1,200°C OF NIOBIUM-TUNGSTEN-TITANIUM AND NIOBIUM-TUNGSTEN-VANADIUM ALLOYS

Alloy No.	Composition						Oxidation conditions at 1,200°C	Test period hours	Test piece surface area (cm ²)	Oxidation rate (mg/cm ² /h)		Remarks
	Atomic %			Weight %						Gain	Loss	
	Nb	W	Ti	Nb	W	Ti						
204	60	20	20	54.6	36.0	9.4	Moist air at 4 l/min	3	3.58	10.6	16.2	Scale spalls
204R	60	20	20	54.6	36.0	9.4		3	4.51	12.1	18.9	
								3	3.56	11.4	16.5	
								3	3.74	10.3	15.9	
205	60	25	15	51.2	42.2	6.6	„	3	3.44	} > 60	—	Test pieces almost completely consumed
								3	3.37			
206	60	15	25	58.4	29.0	12.6	„	3	3.92	13.3	21.5	Scale spalls
								3	4.09	15.4	22.0	
221	50	25	25	44.5	44.0	11.5	„	3	—	11.6	—	Partly adherent scale
								3	—	13.3	—	
222	70	15	15	65.2	27.6	7.2	„	3	—	24.4	—	Partly adherent scale
	Nb	W	V	Nb	W	V						
230	70	20	10	60.8	34.4	4.8	„	1	2.34	> 250	—	Test piece completely consumed
231	70	10	20	69.4	19.7	10.9	„	1	3.75	> 250	—	Test piece completely consumed
232	60	20	20	54.3	35.8	9.9	„	1	2.67	> 250	—	Test piece completely consumed
233	80	10	10	76.0	18.8	5.2	„	3	3.34	> 150	—	Test pieces
								3	3.62	> 150	—	almost completely consumed

— particularly in the case of tantalum, which caused catastrophic oxidation at 1,200°C. It will be appreciated that many more alloys were investigated than it has been possible to describe here where we have confined ourselves to the main thread of the investigation as seen in retrospect.

The next step was to investigate the addition of 5 at. % of other elements to the 80:20:20 niobium-tungsten-titanium alloy in substitution for part of the tungsten and titanium. Oxidation rates are shown in Table IV. Iron, cobalt and nickel were particularly beneficial showing a rate of about two thirds that of the ternary alloy, *i.e.* about 7.5 mg/cm²/h. Beryllium, copper and rare earth metal additions (in the form of Mischmetall) were particularly detrimental.

Variation of the concentration of the fourth addition showed no better results. Replacing the 5 at. % iron by a total of 6 at. % of nickel, iron and cobalt reduced the rate of oxidation from 7.5 mg/cm²/h to 6.8 mg/cm²/h over 3-h tests, which would be of little practical significance.

Taking the niobium-tungsten-titanium-iron (60:17.5:17.5:5 at. %) alloy as the example, further oxidation tests were carried out up to a period of 17 h exposure. Before testing, the arc-melted alloy was heat-treated for 20 h at 1,700°C in vacuum to ensure homogeneity, although there were no grounds to suspect segregation. It was found that the oxidation rate over the longer test period of 17 h was considerably

TABLE IV

COMPOSITION AND 3-HOUR OXIDATION RATES AT 1,200°C IN AIR SATURATED AT ROOM TEMPERATURE OF 60:20:20 ATOMIC % Nb-W-Ti ALLOY WITH ADDITION OF OTHER ELEMENTS

Nb	Composition						Oxidation rate gain in weight mg/cm ² /h	Remarks	
	Atomic %			Weight %					
	W	Ti		Nb	W	Ti			
60	17.5	17.5	Co	56.2	32.4	8.4	Co	7.7	Partly adherent scale
			5.0				3.0		
60	17.5	17.5	Si	57.1	32.9	8.6	Si	9.0	—
			5.0				1.4		
60	17.5	17.5	Al	57.1	33.0	8.6	Al	11.0	—
			5.0				1.4		
60	17.5	17.5	V	56.4	32.6	8.5	V	43.9	—
			5.0				2.6		
60	17.5	17.5	Fe	56.2	32.5	8.5	Fe	7.5	Partly adherent scale
			5.0				2.8		
60	17.5	17.5	Ni	56.2	32.5	8.4	Ni	8.2	„
			5.0				2.9		
60	17.5	17.5	Cr	56.4	32.5	8.5	Cr	14.4	„
			5.0				2.6		
60	17.5	17.5	Zr	55.3	31.9	8.3	Zr	13.7	„
			5.0				4.5		
60	17.5	17.5	Mn	56.3	32.5	8.5	Mn	12.1	—
			5.0				2.8		
60	17.5	17.5	Mg	57.2	33.0	8.6	Mg	9.7	—
			5.0				1.25		
60	17.5	17.5	Zn	56.0	32.3	8.4	Zn	15.5	Scale partly adherent
			5.0				3.3		
60	17.5	17.5	Ag	54.8	31.7	8.2	Ag	14.3	—
			5.0				5.3		
60	17.5	17.5	Be	57.6	33.2	8.7	Be	> 150	Test pieces almost completely consumed
			5.0				0.5		
60	17.5	17.5	B	57.6	33.2	8.7	B	10.6	—
			5.0				0.6		
60	17.5	17.5	Cd	56.7	32.7	8.5	Cd	11.0	—
			5.0				2.0		
60	17.5	17.5	Cu	56.0	32.4	8.4	Cu	> 150	Test pieces almost completely consumed
			5.0				3.2		
60	17.5	17.5	Mo	55.1	31.8	8.3	Mo	10.6	—
			5.0				4.75		
60	17.5	17.5	Ta	52.9	30.6	8.0	Ta	8.8	—
			5.0				8.6		
60	17.5	17.5	Re	52.8	30.5	7.9	Re	9.0	—
			5.0				8.8		
60	17.5	17.5	Pt	52.6	7.9	30.3	Pt	7.6	Scale partly adherent
			5.0				9.2		
60	17.5	17.5	C	57.5	8.6	33.2	C	13.3	„
			5.0				0.62		
60	20	20 + 5 wt. % Mischmetall						> 250	Test pieces completely consumed
50	16.7	16.7	Co	48.9	32.3	8.4	Co	> 100	Almost completely consumed
			16.7				10.35		
50	16.7	16.7	Fe	49.2	32.5	8.5	Fe	20.8	Partly adherent scale
			16.7				9.9		
50	16.7	16.7	Ni	49.1	32.4	8.5	Ni	26.3	—
			16.7				10.0		
50	16.7	16.7	Si	51.7	34.2	8.9	Si	21.5	Partly adherent scale
			16.7				5.2		

reduced to $2.7 \text{ mg/cm}^2/\text{h}$ (compared with $7.5 \text{ mg/cm}^2/\text{h}$ when measured over three hours). Whilst this represents an improvement over unalloyed niobium of over 50 times, it still does not compare with the figures obtained for Nimonic 95 at 950°C , that is to say $0.01 \text{ mg/cm}^2/\text{h}$ and would amount to a deterioration in thickness of approximately 0.030 in. in 100 h at $1,200^\circ\text{C}$ in air.

Small sections of the arc-melted niobium-tungsten-titanium-iron alloy were found to be brittle at room temperature, but considerable resistance to impact with slight deformation was obtained on hammer forging at $1,200^\circ\text{C}$. However, further tests on more massive pieces are being carried out to indicate the possibility of working the alloy.

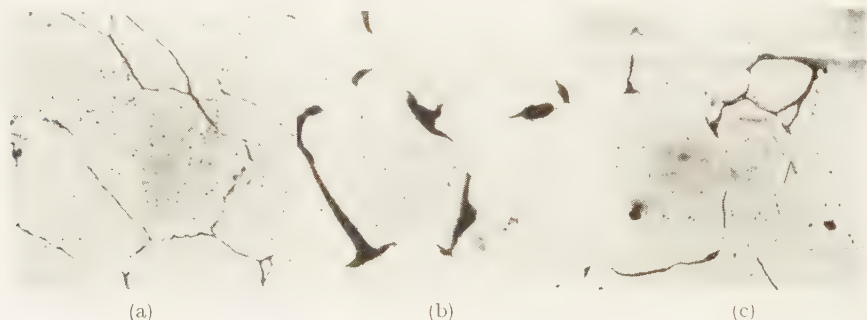


Fig. 3. Photomicrographs of Nb-17.5 at. % W-17.5 at. % Ti-5 at. % Fe alloy showing: (a) the as-melted structure ($\times 250$); (b) after heat treatment for 24 h at $1,700^\circ\text{C}$ in vacuum ($\times 250$); (c) after heat treatment and 17 h exposure to air at $1,200^\circ\text{C}$ showing the surface diffusion layer to the top of the figure ($\times 150$). (All specimens etched in 75:3:6 vol. glycerol-nitric-hydrofluoric acids at 100°C for 5 min.)

Metallographic examination of polished specimens in the arc-melted condition showed a structure consisting of a primary solid solution with a small amount of a second phase in the form of an intergranular film (Fig. 3a). After heat treatment at $1,700^\circ\text{C}$ for 24 h the microstructure was essentially the same as in the as-melted condition, but the intergranular second phase was coarser and tended to form more rounded particles (Fig. 3b) rather than the fine boundary films previously obtained. No appreciable intergranular penetration of oxygen after 17 h exposure to air is indicated by the microstructure, but a surface layer of 0.17 mm average depth can be seen (Fig. 3c). This surface layer is believed to be due to diffusion of oxygen or nitrogen into the metal during oxidation testing and it was in fact found that the total nitrogen content of a test piece after 17 hours exposure to air at $1,200^\circ\text{C}$ had increased from 0.03% to 0.35% , corresponding to a nitrogen absorption of approximately $0.2 \text{ mg/cm}^2/\text{h}$ accounting for roughly one tenth of the observed weight gain.

A microhardness survey across a test piece suggests that the observed surface diffusion layer is the limit of oxygen and nitrogen penetration, in that the hardness drops rapidly from a value of 800 kg/mm^2 in the skin to 575 kg/mm^2 in the body of the specimen. This is shown in Fig. 4.

Two alloys have been reported from the United States of generally similar composition. Both have been developed by the General Electric Co. of America. The first designated G.E. F48 has the composition: 79 at. % niobium-15 at. % tungsten-5 at. % molybdenum-1 at. % zirconium; and gives an oxidation rate of about 12

mg/cm²/h over a 3-h test at 1,200°C. The alloy has moderate ductility hot and develops a partially adherent oxide skin which partly spalls on cooling. The G.E. F50 alloy contains 74 at. % niobium–15 at. % tungsten–5 at. % titanium–5 at. % molybdenum–1 at. % zirconium and has a rather better oxidation resistance of 9.9 mg/cm²/h

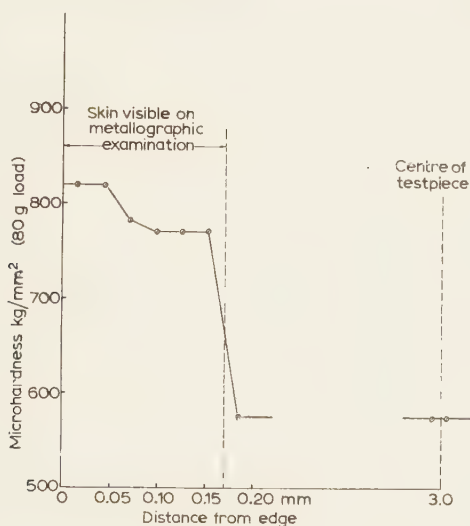


Fig. 4. Microhardness survey across a Nb–17.5 at. % W–17.5 at. % Ti–5 at. % Fe alloy test piece after 17 h exposure to air at 1,200°C.

over a 3-h test at 1,200°C in moist air. This alloy also shows some ductility and had a partially adherent scale. It is interesting to note the general similarity with the niobium–tungsten–titanium–iron alloy described.

MOLYBDENUM — PROTECTION BY COATING

Since the approach to the problem of protecting molybdenum from oxidation by alloying does not seem very promising, particularly because molybdenum oxide is so volatile at relatively low temperatures, attention has been turned to the protection of molybdenum by applied coatings. The work to be presented here has been concerned mainly with the coatings first described by the Climax Molybdenum Company of America².

If molybdenum is used in any high temperature application it will almost certainly be in the form of the 0.45% titanium alloy, which is about twice as strong as pure molybdenum over the temperature range 900–1,200°C. For example the stress for rupture at 100 h for unalloyed arc-cast molybdenum at 980°C is 12,000 p.s.i., whereas for the molybdenum 0.45% titanium alloy it is 28,000 p.s.i.

The creep strength of both the pure metal and the titanium alloy is reduced by recrystallisation below the value for the stress-relieved state. Stress-relieved arc-cast molybdenum shows a stress for rupture in 100 h at 980°C of 22,000 p.s.i., whereas for fully recrystallised material this figure is reduced to 12,000 p.s.i. For applications at temperatures below the recrystallisation temperature — which will range from 950°C upwards depending on the time, temperature and degree of cold work of the starting

material - it may be important to avoid recrystallising the molybdenum during any heat treatment of the applied coat. However, this is not important for applications above this temperature since the molybdenum will be recrystallised in service.

In the main, two coatings have been investigated, a nickel-chromium-boron alloy (as used for hard facing steels) and an aluminium-chromium-silicon alloy, both coatings being applied by metal spraying techniques. Since the nickel-chromium-boron alloy was subsequently shown to be much inferior to the aluminium-chromium-silicon coating with regard to thermal shock resistance and life at the higher temperature of 1,200°C, the description of the process will be concentrated mainly on the latter.

Initially, coatings were applied by the Schori Metallising process using the Schori model 50 acetylene type pistol and ancillary equipment. In this type of metal spraying, powder is lifted from a vibrated hopper by an air stream and carried through the centre of the flame. The fuel gases are normally acetylene and oxygen and the torch nozzle is cooled by a subsidiary stream of air surrounding the flame.

An electric motor is mounted on the roof of a spray booth, connected to an exhaust duct, and this slowly rotates a specimen held vertically in a spring clip. Although it is necessary to change the position of the clip frequently in order to avoid a small uncoated area under the clip, this method of suspension is chosen in preference to consecutive spraying of each side of a static test piece. A thicker deposit is obtained at the edges of the test panels and oxidation due to heating of the reverse side of the test panel being sprayed is avoided. In operation the pistol is directed at the object to be plated at a distance of 8-9 inches.

A disadvantage with the Schori metallising gun for this particular application is the very low efficiency of deposition: as low as 1% on the small test pieces used. Whilst this is no doubt low by a factor of five or so because of the size of the test piece, it is still unacceptably low for any possible production unit. Provision of a cyclone collector could no doubt solve the economic problem, but it would appear technically unsound to pass powder through a flame spraying gun an average of 10-20 times. More suitable from this point of view was the Metallising Equipment Company's gun (Metco Type P Thermospray Gun) which fed powder from a hopper directly into the

TABLE V
ANALYSIS OF ALUMINIUM-CHROMIUM-SILICON ALLOY DEPOSITED ON MOLYBDENUM UNDER DIFFERING CONDITIONS

Reference No.	Deposition conditions	% Insoluble residue in 2.5 N HF acid at 70°C	% Nitrogen
GM.50	Powder before spraying	0.50	0.01
GL.31	Metco Gun. Air-Hydrogen flame	1.00	0.01
GL.25	Schori Gun. Oxy-acetylene flame	1.80	—
GL.23	Metco Gun. Oxy-hydrogen flame	2.10	0.01
GL.24	Metco Gun. Oxy-acetylene flame	6.50	0.11

fuel gas stream; no cooling or conveying gas was required. Using the recommended oxy-acetylene fuel gas mixture in the Metco gun, undesirable oxidation took place and it was necessary to adjust the composition to avoid this. An air-hydrogen mixture was finally used. Oxidation of the coating material on spraying the aluminium-chromium-silicon coating is shown in Table V where the portion of the coating insoluble in 2.5 *N* HF at 70°C is taken to be a measure of the oxygen content. The nitrogen content is also shown.

The composition of nickel-chromium-boron hard facing alloy, commercially available as Colmonoy 6 is as follows: 72% nickel-15.5% chromium-3.0% boron-4.5% silicon-4.0% iron-1% carbon.

Aluminium-chromium-silicon alloy was prepared by adding 20% aluminium powder (—120 mesh) to —120 mesh 60:40 chromium-silicon alloy prepared by aluminothermic reduction. A typical chromium-silicon alloy contained 61.7% chromium-34.9% silicon-1.95% aluminium-0.6% iron. The aluminium powder was obtained from Murex Limited, Grade B2 99/99.5% purity.

Test pieces for spraying were cut from 0.050 in. molybdenum or niobium 0.45% niobium sheet. Corners and edges were rounded with a file to assist in the adhesion of metal powders during spraying. Immediately before spraying all surfaces of test pieces were roughened by sand blasting followed by chemical cleaning in hot 50% hydrochloric acid followed by washing in tap water and demineralised water, and drying with acetone.

The coatings in the as-sprayed condition are extremely porous and only mechanically bonded and must be bonded metallurgically before use. This fusion treatment is extremely important in determining the life of the coating; too low a temperature results in an undersintered structure with excessive porosity and too high a temperature results in excessive fluidity and consequent uneven flow.

Whilst the nickel-chromium-boron alloy was found to fuse satisfactorily in hydrogen at 1,100°C (one hour treatment) difficulty was experienced in providing hydrogen of sufficient purity to avoid oxidising the aluminium in the aluminium-chromium-silicon coating. The final technique adopted for this alloy was to fuse test pieces in a vacuum of $5 \cdot 10^{-5}$ — $1 \cdot 10^{-4}$ mm of Hg for 2 h at 1,100°C. Specimens were coated with an alumina-alcohol slurry before fusing to protect the coating where it touched the alumina supporting tiles.

Oxidation testing was essentially as described for niobium alloys, except that dry air was used since the breakdown of the coating, when it occurred, led to catastrophic oxidation of the underlying molybdenum. The rate of oxidation was unimportant, the life of the coating being the determining factor.

In the apparatus used for thermal shock testing a sample $3\frac{3}{4} \times 1 \times 0.050$ in. is supported at one end in a clamp actuated by an air piston and alternately heated in a muffle at 1,000°C and cooled in a blast of air. The temperature cycle is shown in Fig. 5, where it can be seen that cooling to room temperature occurs in about five seconds. The results obtained on this machine have proved extremely useful in assessing the relative thermal shock resistance of various coatings.

Nickel-chromium-boron coatings gave a very satisfactory performance at 1,000°C. In life testing at constant temperature, lives of up to 500 h being regularly obtained. However, at 1,150 or 1,200°C, failure occurred after 20 hours or so, even after prior exposure in air at lower temperatures when diffusion of niobium into the coating

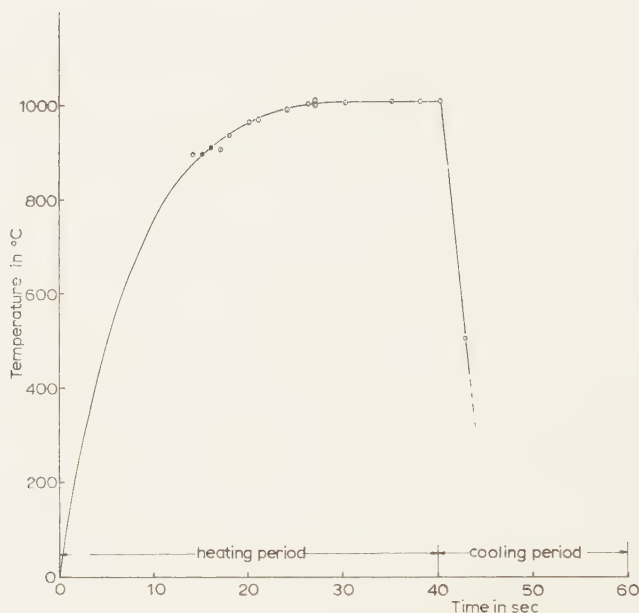


Fig. 5. Thermal shock test heating and cooling cycle.

would be expected to raise its melting point. Thermal shock tests were also disappointing, the coated specimens withstanding only from 4-20 thermal shock cycles and becoming seriously distorted under test as shown in Fig. 6.

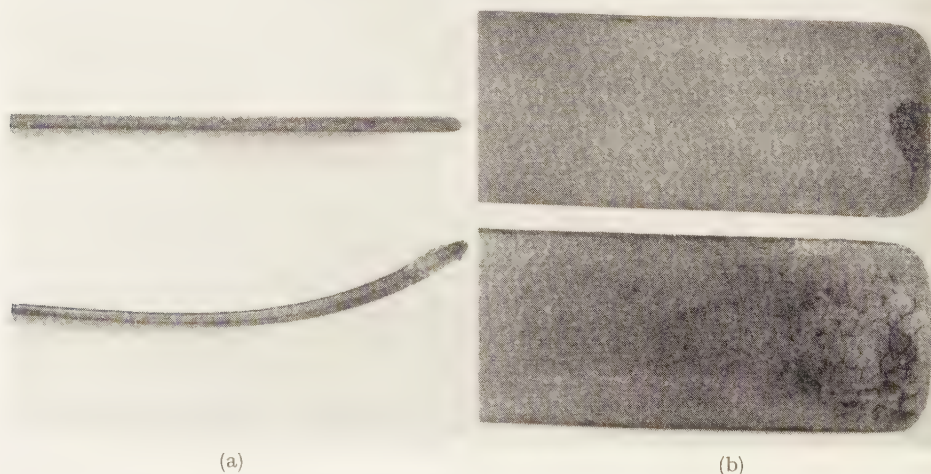


Fig. 6. Coated molybdenum specimens after thermal shock testing. (a) distorted specimen coated with nickel-chromium-boron alloy (below) compared with undistorted specimen coated with aluminium-chromium-silicon alloy (above) and (b) typical failures in the nickel-chromium-boron coating (below) and aluminium-chromium-silicon coating (above).

Preliminary tests on molybdenum coated with a single layer of aluminium-chro-

aluminium-silicon gave promising though somewhat variable results ranging from 30-302 h life at 1,000°C and 50-75 h at 1,200°C. Micro examination of the coating — a photomicrograph is shown in Fig. 7a of a coating after 75 h exposure at 1,200°C — shows very good bonding of the coating to the molybdenum but shows a series of vertical fissures through the coating. At a larger magnification Fig. 7b one vertical fissure is shown on failure of the test piece after 300 h in air at 1,000°C.

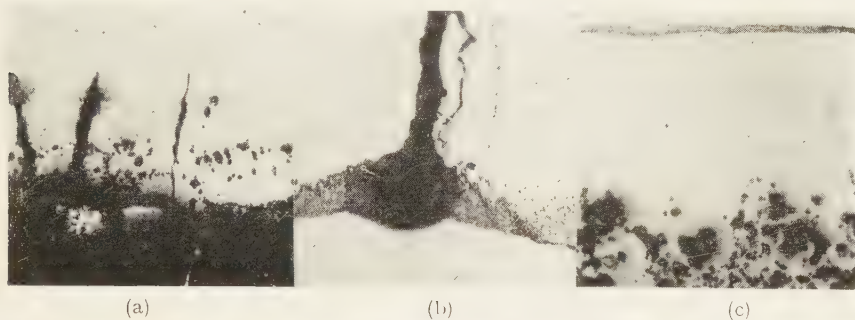


Fig. 7. Photomicrographs of molybdenum coated with aluminium-chromium-silicon coatings: (a) showing typical cracks in a single coating (specimen failed after 300 h at 1,000°C) ($\times 200$) (b) an enlarged view of one crack ($\times 750$) and (c) double layer of aluminium-chromium-silicon showing the absence of cracks penetrating through the coating ($\times 200$).

In order to reduce the effect of vertical fissure which appears to be characteristic of this alloy coating, further test pieces were produced on which a second layer of aluminium-chromium-silicon alloy was applied after vacuum fusion of an initial layer of approximately 0.010 in. Lives from 375-425 h at 1,000°C and 125-150 h at 1,200°C were obtained on these test pieces, the microstructure of which is shown in Fig. 7c. Subsequent experience in applying aluminium-chromium-silicon coatings led to the stage where the average lives of samples ranged from 400-500 h at 1,000°C, 1250-300 h at 1,100°C and 150-200 h at 1,200°C. Although this performance is somewhat inferior to that of the nickel-chromium-boron alloy at 1,000°C the aluminium-chromium-silicon coating is much superior in its resistance both to oxidation at 1,200°C, and to thermal shock. Whereas the nickel-chromium-boron coating gave a life of only 4-20 thermal shocks from 1,000°C to room temperature, the aluminium-chromium-silicon coating withstood 280-300 thermal shocks over the same temperature range before failure and showed little or no distortion, as shown in Fig. 6. It was found that thermal shock tests interrupted with periods of exposure to oxidation at a constant temperature of 1,000°C gave more consistent results than tests with continual thermal shock presumably because it was so much easier to determine exactly when failure occurred, at least to within one group of thermal shocks. It was finally decided to standardise the test giving a group of 20 thermal shocks followed by 6 h at a constant temperature of 1,000°C.

The life of specimens on thermal shock testing was dependent on whether the test was conducted with an initial group of thermal shocks, or an initial exposure to air at 1,000°C. Fig. 8 shows a record of weight gains of samples during interrupted thermal shock tests under both conditions. The initial loss in weight of specimens undergoing a group of thermal shocks before exposure at constant temperature is due to the

exudation and loss of a liquid phase in the coating which does not occur when exposure at constant temperature is the first treatment. This alters the composition of the coating and affects the life. Therefore all parts coated with the aluminium-chromium-silicon coating should be given a 6 h exposure to air at $1,000^{\circ}\text{C}$ before use, this also constituting a useful proving test to guard against a possible defect in the coating.

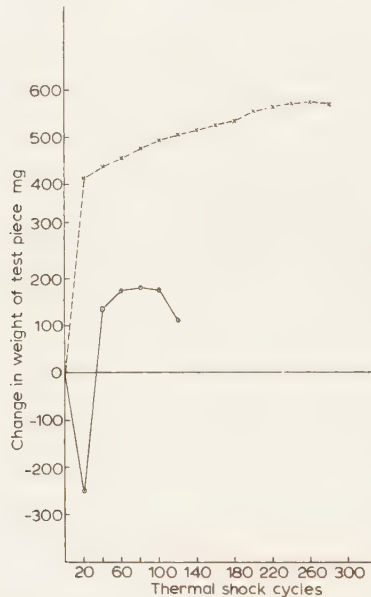


Fig. 8. Results of interrupted thermal shock tests on molybdenum test pieces coated with aluminium-chromium-silicon coating, showing specimens given an initial treatment of a group of thermal shocks as compared with specimens initially exposed to oxidation at $1,000^{\circ}\text{C}$ for 6 h. -- x -- With initial 6-h exposure to oxidation; — o — with initial group of 20 thermal shocks.

The maximum life of the coating is believed to be determined by the diffusion of molybdenum through the coating which is very extensive as seen in Table VI. A certain amount of diffusion would seem to be necessary to stabilise the coating for operation at the higher temperatures, but if this could be limited, longer lives should be obtained. Some work has been carried out on the use of diffusion barriers such as gold, nickel, and silicon monoxide, but no improvement in oxidation resistance was found.

TABLE VI

DIFFUSION OF MOLYBDENUM THROUGH ALUMINIUM-CHROMIUM-SILICON COATINGS

Exposure period (hours)	Test temp. ($^{\circ}\text{C}$)	Molybdenum content of coating %
(1) Vac. fused at $1,100^{\circ}\text{C}$ for total of 4 h (2 h each coat)	—	21.5
(2) As (1) plus 398 h in air	1,000	33.2
(3) As (1) plus 288 h in air	1,100	38.8
(4) As (1) plus 206 h in air	1,200	46.4

From the results presented here, it will be realised that these coatings are not likely to be serviceable at temperatures above $1,200^{\circ}\text{C}$. Attempts have been made to coat molybdenum with many other materials of higher melting point but so far no success has been obtained.

Not surprisingly there have been some failures in the coatings which have been difficult to overcome, sometimes transitory in nature and difficult to understand. One which has been the incidence of blistering, which whilst apparently not affecting the life, renders the coating unsightly and of a surface roughness which is likely to be unacceptable aerodynamically. Blisters form in the top coat only and do not affect the first coat. Cleaning between treatments and similar precautions do not have any effect, but there is some evidence that blistering may be reduced by altering the ratio of coating thicknesses to say 0.010 for the first coat and 0.005 in. for the second coat.

PROTECTIVE COATINGS ON NIOBIUM

In parallel with the work on protection of niobium from oxidation by alloying, some experiments have been carried out on protection by coating. The techniques used in general have been the spraying methods used and described for molybdenum. In fact, the first coatings to be tried were the nickel-chromium-boron and the aluminium-chromium-silicon alloys as used for molybdenum. However, results were not so good and other alloys have been tried, the best so far being an 20:40:40 aluminium-iron-silicon alloy.

The spraying alloy consisted of a mixture of 20% aluminium with 80% of a 50:50 iron-silicon master alloy. Test pieces coated with about 0.015 in. in the sprayed condition gave a uniform fused coating of about 0.005 in. when heat-treated at $1,200^{\circ}\text{C}$ for one hour. A typical test piece coated with a single coat gave a life of 200 h at $1,000^{\circ}\text{C}$. Double coating the test pieces resulted in no improvement in the oxidation life. Considerable diffusion of niobium into the test piece occurred during the fusion treatment, up to about 45% and this may well contribute to the short life.

Many other alloys have been tried without success to improve upon this very short life. Alloys such as the aluminium-chromium-silicon composition as used on molybdenum, and alloys of aluminium, molybdenum, chromium, cobalt, nickel, silicon and boron of which a 20:57:23 aluminium-chromium-boron is typical have given some protection, but not even to the extent of the iron-silicon-aluminium alloy described. Many other alloys have been tried and found to give no protection.

DISCUSSION

Considering the amount of work that has been carried out on the protection of niobium by alloying it now seems unlikely that an alloy will be produced which is oxidation-resistant in its own right. Alloys from the United States such as the General Electric E. F48 and F50 alloys have a similar oxidation resistance to the niobium-titanium-tungsten-iron alloy described and in fact are generally similar in composition. It would seem that it will be necessary to apply coatings to the alloy to give general protection, using the enhanced oxidation resistance of the alloy as a means of delaying breakdown of the underlying metal should failure of the coating occur. This will also enable more attention to be paid to the strengthening of the metal by alloying. It therefore seems necessary to concentrate more on improving coating techniques for niobium and its

alloys since the position is far from satisfactory. One promising line may be the coating of niobium or niobium alloys with niobium aluminide, either by spraying, by dipping in aluminium or by aluminising, since such compounds have been reported as having a high resistance to oxidation at 1,200°C.

In the case of molybdenum, a lot of work has been done both here and in the United States on the protection of molybdenum with a variety of techniques but it cannot be said that the results are entirely successful. One of the drawbacks is the catastrophic rate of oxidation of the molybdenum should the coating fail.

These remarks have been concerned mainly with those applications requiring relatively long term protection at temperatures in the range 1,000–1,200°C such as for gas turbine blades. There are, however, many other applications, for instance rocketry, where short term protection is required at these or higher temperatures, and the properties required in the protected metal may be somewhat different.

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OXIDATION BEHAVIOUR OF NIOBIUM-CHROMIUM ALLOYS

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SUMMARY

An examination of the properties of chromium niobate indicates the possibility of producing an oxidation-resistant niobium-chromium alloy. A series of such alloys has been prepared and subjected to oxidation tests. Tests on one of these alloys in different atmospheres reveal a considerably higher oxidation rate in air than in oxygen. A possible mechanism is suggested to account for this phenomenon.

INTRODUCTION

A necessary condition for self protection of a niobium-rich alloy against oxidation at elevated temperatures is the formation of an adherent self-healing oxide coating on the surface. The structure of this oxide should provide as complete a barrier as possible to the diffusion of oxygen inwards and metal cations outwards. The adhesion of the oxide is determined firstly by the volume-ratio of the oxide and underlying alloy and secondly by their relative thermal expansions. For good adhesion, the maximum permissible volume ratio resulting from application of the Pilling-Bedworth relationship is 1.15. However, the value for chromic oxide on chromium is 2.07 and silica on silicon 1.88, and since both oxides are protective, this proposal seems rather pessimistic and a volume ratio of 2 may well be acceptable if other factors are favourable. The high temperature form of niobium pentoxide, on the other hand, has a volume ratio of 2.7, which explains why the oxide skin flakes away from niobium as soon as appreciable quantities of this highest oxide have formed.

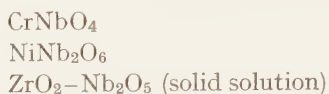
An important factor concerning adhesion of the oxide, especially when subjected to thermal shocks is its thermal expansion coefficient. This should be as near to that of the parent metal as possible.

Finally, the best diffusion barrier is likely to be provided by the more complex single or multiple oxide structures, as is found for example with the spinel-type structures formed on nickel-chromium alloys and austenitic heat-resisting steels.

INVESTIGATION OF DOUBLE OXIDES

In a preliminary study various powder mixtures of Nb_2O_5 and other metal oxides were prepared, pressed and sintered, and the resultant material examined by X-ray diffraction. From this study three double oxides were found which it was thought

might provide good diffusion barriers. These three double oxides are:



Bars of these combinations, suitable for use in a conventional dilatometer, were prepared. The appropriate proportions of powder were thoroughly mixed by tumbling for 20 h, pressed at room temperature in a steel die with cavity dimensions $\frac{1}{4}$ in. $\times$ $\frac{1}{4}$ in. $\times$ $1\frac{1}{2}$ in. and the resulting bars sintered for 15 h at $1,300^\circ\text{C}$ in air. Dilatometer curves over the temperature range $20^\circ\text{--}1,000^\circ\text{C}$ showed the following mean thermal expansion coefficients.

CrNbO ₄	5.9 p.p.m./°C
NiNb ₂ O ₆	3.0 p.p.m./°C
ZrO ₂ –Nb ₂ O ₅	4.5 p.p.m./°C

The curve for CrNbO₄ was not, however, smooth, but showed a sudden steepening just below 800°C . To ascertain whether this was due to a phase change, the material was studied in a high temperature X-ray diffraction camera. No new phase appeared to be formed. The mean thermal expansion coefficient of CrNbO₄ measured by this method over the temperature range $20^\circ\text{--}840^\circ\text{C}$ was 5.1 p.p.m./°C, which is in reasonable agreement with the dilatometer figure averaged over $20^\circ\text{--}1,000^\circ\text{C}$.

It appeared, therefore, that on the basis of its thermal expansion, CrNbO₄ was the most promising of the three double oxides studied, although the expansion coefficient of the parent alloy had the considerably higher value of 9 p.p.m./°C.

The reported structure of the niobate CrNbO₄ has been confirmed at Caswell Laboratories. Its tetragonal atomic arrangement contains one molecule per unit cell of dimensions $a = 4.64 \text{ \AA}$, $c = 3.013 \text{ \AA}$ at room temperature (*i.e.* $65 \text{ \AA}^3$ volume). The volume ratio with respect to its theoretical parent alloy (50–50 atomic % Cr–Nb), was calculated to be 2.1. To estimate the extent to which it might hinder diffusion, a comparison was made with a spinel structure.

	Vol. per molecule ($\text{\AA}^3$)	Number of atoms/molecule	
		Metal	Oxygen
A typical spinel structure ($\text{MeO.Mt}_2\text{O}_3$)	70	3	4
CrNbO ₄	65	2	4

From this the niobate structure appears to be reasonably promising as a diffusion barrier.

On all three criteria, thermal expansion, volume ratio and structure, there should then be some prospect of a useful degree of self-protection in a 50–50 atomic % Cr–Nb alloy, the theoretical parent of CrNbO₄.

PREPARATION AND OXIDATION OF NIOBIUM–CHROMIUM ALLOYS

Although the 50–50 atomic % Nb–Cr binary was of immediate interest, initial oxidation results from this material suggested that lower chromium contents down

say 20 atomic %, should be explored to see how far reasonable oxidation properties could be achieved without a severe brittleness problem. Accordingly, samples containing 50, 45, 40, 35, 30 and 25 atomic % of chromium were prepared. The preparation of the alloys was carried out in an atmosphere of argon, using the cold hearth R.F. melting technique developed at CASWELL¹. This melting technique is very similar to arc-melting except that R.F. heating is used instead of an arc. The specimens were melted a second time after inversion of the specimen, in order to ensure complete melting. This was followed by heating to 1,500°C under a vacuum of $5 \cdot 10^{-5}$ mm Hg for 30 min in order to facilitate some degree of homogenisation.

Chemical analysis checks on the final composition of some of these alloys showed that, unlike sintering processes involving chromium, negligible loss of this metal occurred when this method of preparation was used.

Oxidation tests on these niobium-chromium binaries were carried out using a Anton Recording Balance in conjunction with a platinum furnace. The design was such that the atmosphere could be varied as required. The following test procedure was employed. The alloy was heated in the platinum furnace until a temperature of 1,100°C was reached, during which time a stream of argon flowed over the specimen at the rate of 0.4 l/min, thus preventing any oxidation. On reaching a temperature of 1,100°C a stream of dried oxygen flowing at 0.4 l/min, was substituted for the argon. Weight changes were recorded continuously by the balance. The normal oxidation tests were of 17 h duration. A longer confirmatory test of 65 h was carried out where necessary.

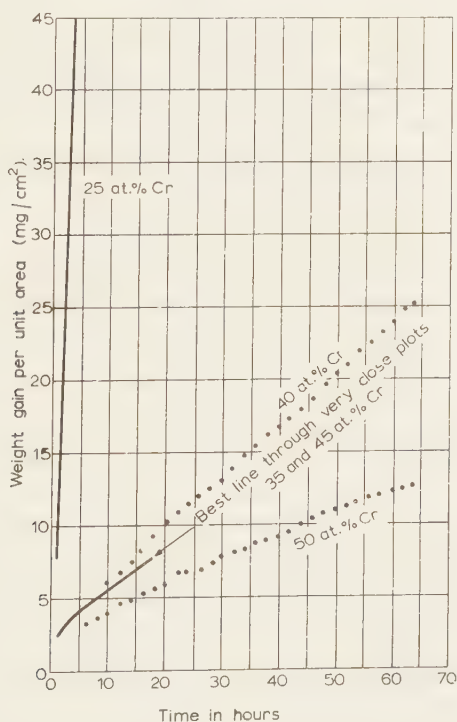


Fig. 1. Oxidation of various niobium-chromium alloys in oxygen at 1,100°C.

The curves of weight gain per unit area against time under these conditions, are presented in Fig. 1. In order to ascertain the type of oxidation law operating, the results are plotted logarithmically in Fig. 2. This plot will be linear with a slope of $1/x$ if a single power law of the following type is obeyed:

$$W^x = at + c$$

where W = weight gain/unit area

t = time

a and c are constants

The results obtained for alloys with chromium contents between 35 and 50 atomic %, give values of x between 1 and 2. The type of oxidation law is thus intermediate between linear and parabolic. The rapid oxidation rate of the 75–25 atomic % Nb–Cr binary suggests that for a simple binary alloy, the minimum chromium content for reasonable oxidation resistance is about 35 atomic %.

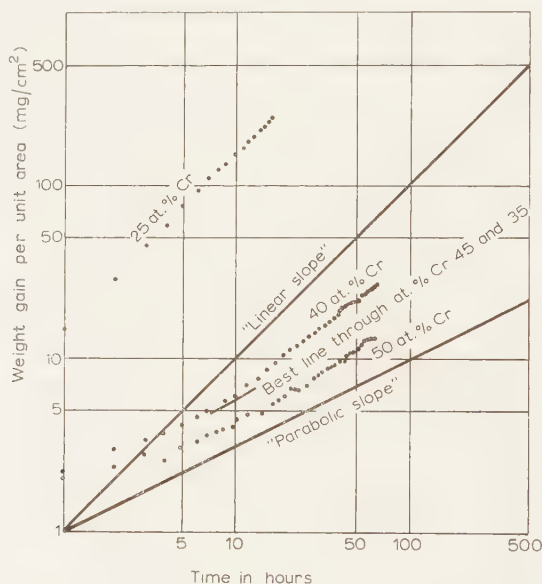


Fig. 2. Oxidation of various niobium–chromium alloys in oxygen at 1,100°C.

X-ray diffraction analysis of the oxide film from the alloy containing 50 atomic % chromium, which is the theoretical parent of CrNbO_4 , showed that this double oxide was formed during oxidation although appreciable amounts of H-type (high temperature form) Nb_2O_5 were also present. The presence of this excess Nb_2O_5 is undoubtedly due to preferential oxidation of niobium which would be expected from a consideration of the free energy of formation of Nb_2O_5 and Cr_2O_3 (–373 kcal/mole for Nb_2O_5 and –180 kcal/mole for Cr_2O_3 at 1,000°C)².

For further study a composition of 65–35 atomic % Nb–Cr was chosen. Any increase in the chromium content does not improve oxidation resistance appreciably, but is likely to accentuate the problem of brittleness associated with chromium-containing alloys.

PRELIMINARY OXIDATION OF A 65-35 ATOMIC % Nb-Cr ALLOY

Although more severe oxidation was expected to occur in pure oxygen than in air, the assumption has been shown to be incorrect in the case of this alloy. Fig. 3 shows weight gain/cm² plotted against time for oxidation tests carried out in air and oxygen. All tests were conducted at 1,100°C in the thermobalance with gas flows of 0.4 l/min. After 17 h the weight gain/cm² in air was four to five times that in oxygen and the weight gain after 60 h was even greater. To attempt to explain this phenomenon the effect of nitrogen on the oxidation of the 65-35 atomic % Nb-Cr binary was investigated in more detail.

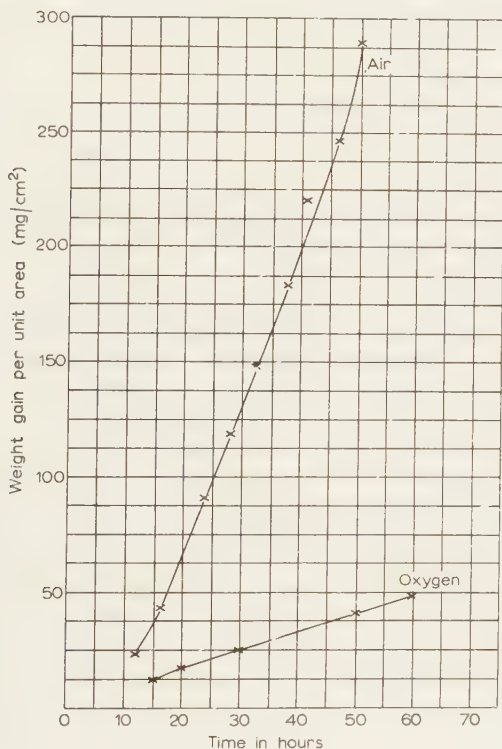


Fig. 3. Oxidation of a 65-35 at. % niobium-chromium alloy in air and oxygen at 1,100°C.

THE EFFECT OF NITROGEN ON THE OXIDATION RATE OF A 65-35 ATOMIC % Nb-Cr ALLOY

Experimental

A series of oxidation tests was carried out in oxygen-nitrogen mixtures containing between 10 and 96 vol. % of nitrogen. For all tests hearth-melted specimens were used. The tests were carried out in the thermobalance for 17 h at a temperature of 1,100°C using hearth-melted specimens. The composition of the gas mixture was controlled by needle-valves and the total rate of flow maintained at 0.4 l/min. The gases were mixed and dried with anhydrous before entering the reaction chamber. The reaction of pure nitrogen with the 65-35 atomic % Nb-Cr alloy for 17 h at

1,100°C was performed in a specially constructed furnace to eliminate the possibility of oxygen contamination due to back diffusion of air. High purity nitrogen dried by anhydron and passed over heated niobium to remove traces of oxygen was used.

Two tests were carried out in the thermobalance involving pretreatment of hearth-melted specimens at 1,100°C in nitrogen, directly followed by treatment in pure oxygen at the same temperature. One test consisted of a 17-h run in nitrogen followed by a further 40 h in oxygen, whilst in the second one, the run in nitrogen was limited to 2 h, again followed by 40 h in oxygen. The rate of flow of the gases was 0.4 l/min in each case.

A further oxidation test using the same temperature and gas flow conditions was performed in the thermobalance using a 50-50 vol. % mixture of argon and oxygen. The test was carried out to confirm that the behaviour described was associated with the presence of nitrogen.

One of the factors causing the increased oxidation rate of 65-35 atomic % Nb-C alloy when nitrogen is introduced into an oxygen atmosphere may well be the ability of nitrogen to diffuse into the alloy more readily than oxygen. This possibility has been investigated by micro-hardness measurements.

Four hearth-melted specimens were used for these experiments, two being treated in oxygen and two in nitrogen. In each case the treatment was carried out for a period of 17 h at 1,100°C using a gas flow of 0.4 l/minute. The specimens were then sectioned and the surface carefully polished. A line of micro-hardness measurements was taken perpendicular to the surface of the alloy. The measurements were made using a Leitz Miniload Hardness Tester with a 300 g load.

Results

The results of the oxidation tests carried out in various oxygen-nitrogen mixtures are presented in Fig. 4. The graph shows that the weight gain rises sharply at either end of the plot to a value of about 40 mg/cm² when the proportion of either nitrogen or oxygen is very small in the gas mixture. This weight gain then scarcely varies for any other proportion of the mixed gases. From these results it would appear that the

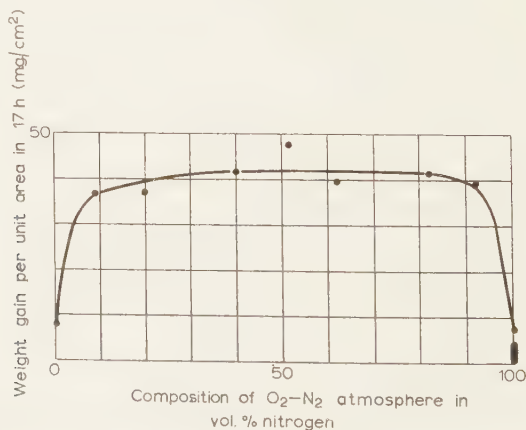


Fig. 4. Reaction of a 65-35 at. % niobium-chromium alloy with different oxygen-nitrogen mixtures at 1,100°C.

nitrogen is acting as a catalyst, only a very small amount being needed to increase the rate of reaction by four or five times.

The test in pure nitrogen shows a weight gain comparable to that in pure oxygen (the value is plotted in Fig. 4). The surface of the specimen appeared to be barely polished, but a micrograph (Fig. 5) of a section through the nitrided alloy shows that a thin film was formed. The existence of this film was confirmed by microhardness measurements which showed the presumed nitride layer to be considerably harder than the alloy itself. It was possible to scrape a small amount of "nitrided" film from the surface of the specimen and this was examined by X-ray diffraction. However, it was not possible to interpret the X-ray patterns, neither niobium nor chromium nitride being present. It is probable that a complex mixed niobium-chromium nitride was formed.



Fig. 5. 65-35 at. % Nb-Cr binary after treating with nitrogen at 1,100°C for 17 h. Etched aqua regia + 20% HF, showing a thin compact nitride layer. The microhardness indentations show this layer to be harder than the alloy itself. ($\times 200$)

The results of the oxidation tests carried out after pretreatment in nitrogen, are shown in Fig. 6. The oxidation curves given commence at the time the oxygen was introduced. In the first test (17 h pretreatment in nitrogen), curve A shows that the initial reaction rate in oxygen was 72 mg/cm² in the first 17 h (*i.e.* much above the rate normally observed in pure oxygen). However, after 21 h there was a distinct and marked decrease in the reaction rate, as can be seen from the graph. No such marked change is apparent in curve B (2 h pretreatment in nitrogen), although a slight increase in reaction rate is perceptible after about 15 h.

The oxidation rate in a 50-50 vol. % mixture of oxygen-argon proved to be of the same order as that in pure oxygen, thus confirming that a reduction in the partial pressure of oxygen does not increase the oxidation rate.

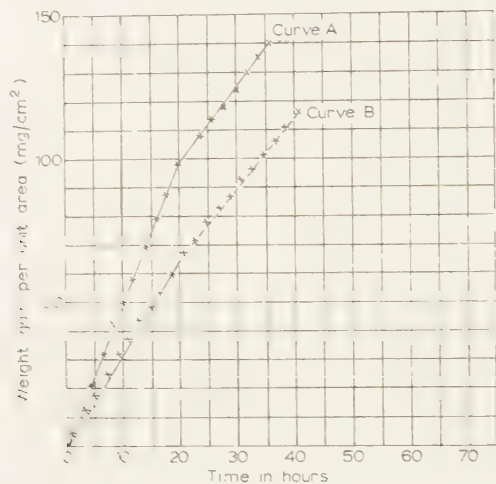


Fig. 6. Reaction of a 65-35 at. % niobium-chromium alloy at 1,100°C following pretreatment with nitrogen.

Fig. 7 shows the result of hardness measurements taken on the specimens oxidized in oxygen and air. Although the curves are somewhat variable, they do show that the nitrogen penetration exceeds that of oxygen.

A general hardness figure for a 65-35 atomic % Nb-Cr alloy in the "as-melted" condition is 900-1,000 V.P.N. For the alloys treated in oxygen the hardness figure falls to this value at depths of 50 μ (curve A) and 100 μ (curve B), whereas for the

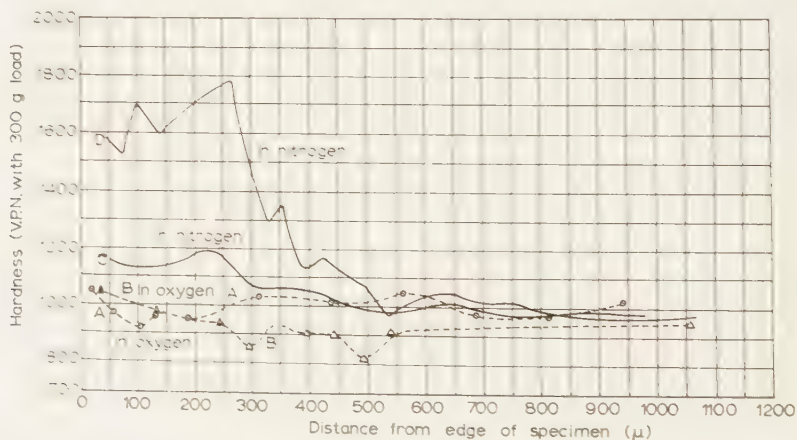


Fig. 7. Hardness of a 65-35 at. % niobium-chromium alloy after treatment in oxygen and nitrogen.

alloys treated in nitrogen the hardness exceeds 1,000 V.P.N. until depths of 450 μ (curve C) and 550 μ (curve D) are reached.

Discussion

The above results show quite conclusively that the increase of oxidation rate in oxygen-nitrogen mixtures over that in pure oxygen is due to the catalytic action of nitrogen. It has been shown by hardness measurements that nitrogen is capable of faster diffusion into this alloy than is oxygen. This would suggest that the "nitride" is formed before the oxide. It has been shown by X-ray diffraction of the film formed by air oxidation that no nitride is present. The film consists only of CrNbO_4 and γ -type Nb_2O_5 . Thus it would appear that the conversion of nitride to oxide is very fast.

The results of oxidation following pretreatment in nitrogen (Fig. 6) may be explained as follows. Pretreatment in nitrogen for 17 h allows nitrogen to diffuse into the alloy to a considerable depth and this facilitates subsequent attack by oxygen, thus giving a fast reaction rate (curve A, Fig. 6). However, when oxidation has proceeded so far that the complete shell of "nitrided" alloy has been oxidised, no further catalysis takes place, and a substantial decrease in the rate of reaction results. This state of affairs is apparently reached in 20 h in this instance. The rate of reaction in the latter stages (after 20 h) is still greater than in pure oxygen, but this is probably due to traces of "nitride" still remaining, perhaps as a result of regeneration of nitrogen on oxidation of the "nitride".

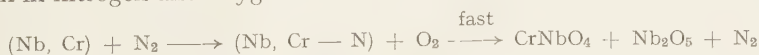
It was in an attempt to confirm this hypothesis that the second test was undertaken, with 2 h pretreatment in nitrogen. It was thought that by considerably reducing the pretreatment time in nitrogen, the changes in reaction rate would occur after a shorter time. Although the overall reaction rate in oxygen (curve B) was much lower than in the previous test, no marked changes in the rate occurred, but a very slight decrease after some 15 h was observed. It may be noted, however, that the complete slope of curve B is the same as that of the latter portion of curve A, which seems to suggest that the diffusion of nitrogen into the alloy during the 2 h pretreatment was only slight. This being the case, no very marked change in rate of reaction with oxygen could be expected.

The exact nature of the catalytic action of the nitrogen is not known, but two suggestions can be put forward. The first is that the fast prediffusion of the nitrogen allows much easier and faster diffusion of oxygen, thus giving a faster rate of reaction. The following hypothesis is preferred, however. The nitrogen diffuses through the alloy, forming a complex "nitride" which is immediately oxidised, this conversion of "nitride" to oxide being much faster than the simple oxidation of alloy to oxide. Two possible oxidation mechanisms can, therefore, occur depending on the atmosphere.

Oxidation in pure oxygen



Oxidation in nitrogen and oxygen



It is in fact possible that the complete reaction of alloy via "nitride" to oxide is faster than alloy to oxide direct.

It can be seen from Fig. 3 that the reaction rate of the 65-35 atomic % Nb-Cr alloy with air at 1,100°C increases with time. A possible explanation is that the thin semi-protective film primarily formed on the alloy surface becomes more and more cracked and porous as the oxidation progresses.

CONCLUSIONS

The results show beyond doubt that the presence of nitrogen has a very adverse effect on the oxidation rate of a 65-35 atomic % Nb-Cr (the effect probably occurring with a whole series of Nb-Cr alloys). As neither niobium nor chromium has a faster oxidation rate in air than in oxygen, it must be concluded that it is the presence in the Nb-Cr alloy of either the solid solution (chromium in niobium) or the compound (NbCr₂) or both, which enables nitrogen catalysis of the oxidation process to occur.

ACKNOWLEDGEMENTS

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THE EFFECT OF OXYGEN PRESSURE ON THE HIGH TEMPERATURE
OXIDATION OF TANTALUM

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SUMMARY

The pressure dependence of the linear rate constant for the oxidation of tantalum has been investigated in the temperature range 600°–900°C and the pressure range 1–760 mm Hg. The results confirm that the controlling step is preceded by an equilibrium adsorption process, as suggested by FASSELL *et al.*^{5,6}, and indicate that at low pressures the rate-controlling step depends on the square root of the oxygen pressure. At lower temperatures and higher pressures another process controls the rate, which varies linearly with pressure. Possible reaction mechanisms are proposed to account for the observations.

INTRODUCTION

JULBRANSEN AND ANDREWS¹ found that the oxidation of tantalum in the temperature range 250°–450°C follows a parabolic rate law, and DRAVNICKS² found a parabolic rate law applies also at 500°C at an oxygen pressure of 0.5 mm Hg. WABER, STURDY, ROUSE AND TIPTON³ considered that the oxidation is parabolic in the range 320°–350°C, but that in the range 220°–320°C the experimental points were better fitted by a logarithmic law; but later WABER⁴ replotted these points and obtained a cubic law. In general, at all temperatures from 500°C to 1,500°C the oxidation follows a linear rate law^{5,6,7}. At the lower temperatures in this range there is a short initial non-linear portion, and the oxidation rate curve above 1,000°C is rather more complicated than a simple straight line⁸.

FASSELL *et al.*^{5,6} have studied the pressure and temperature dependence of the linear rate constant. An Arrhenius plot of the logarithm of the rate constant versus the inverse of the absolute temperature shows three main regions. In the range 600°–600°C the rate increases normally with temperature, and is independent of pressure variations in the range 0.5–40 atmospheres. Between 600°C and 800°C the rate drops slightly with increasing temperature and is strongly pressure-dependent. Above 800°C the rate increases with increasing pressure at low pressures, but as the pressure increases the rate of increase of the rate constant decreases and eventually at high pressures the rate is independent of pressure. Above 800°C the rate again increases normally, but still shows strong pressure dependence. Because of the rapidity of the oxidation, it was not possible to determine the exact form of the pressure dependence above 800°C.

FASSELL showed that it was possible to explain both the temperature and pressure dependences of the reaction by assuming that

(1) the rate of the rate-determining process is a function of the oxygen concentration at some interface, and

(2) the oxygen concentration at this interface is determined by an equilibrium adsorption process.

On this model the interface concentration is given by a Langmuir isotherm, so that the fraction of the surface covered with adsorbed oxygen θ is given by

$$\theta = \frac{ap}{1 + ap}$$

where p is the oxygen pressure, and a is a constant. At high pressures, $ap \gg 1$ and $\theta \cong 1$ and is independent of pressure. At low pressures $ap \ll 1$ and $\theta \cong ap$, so that the surface concentration depends linearly on pressure. The temperature dependence of θ at constant pressure is given by

$$\frac{\theta}{1 - \theta} = \text{const. } (T)^{-5/2} e^{E/KT}$$

where T is the absolute temperature, E is the heat of adsorption per molecule at 0°K , and K is Boltzmann's constant. As $T \rightarrow 0$, $\theta \rightarrow 1$; and as $T \rightarrow \infty$, $\theta \rightarrow 0$. Thus at constant pressure, the surface concentration decreases with increasing temperature.

At low temperatures therefore the surface is saturated for normal pressures and the rate is independent of pressure. The temperature dependence of the rate is the same as that of the rate-controlling interface reaction. As the temperature is raised, a point is reached at which at constant pressure the surface concentration decreases with increasing temperature. The temperature dependence of the reaction rate is thus the resultant of two terms: the increasing rate per atom of the interface reaction, and the decreasing concentration of atoms available. The reaction rate will thus show less temperature dependence than at lower temperatures, but the exact amount less depends on the relative temperature dependences of the two processes. Eventually at high temperatures the surface concentration of oxygen will be the same as the atmospheric concentration and thus independent of temperature. The temperature dependence of the reaction rate will again be that of the interface process.

If the rate-determining step is dependent on the n th power of the interface concentration, then clearly at low pressures the oxidation rate will depend on the n th power of pressure, whereas at high pressures the rate will be independent of pressure. In their analysis FASSELL *et al.* tacitly assume that the rate of the interface step depends linearly on the concentration, i.e. that $n = 1$. In the pressure range they were examining, the exact value chosen for n would not have affected the general shape of the curves. In order to determine the oxidation mechanism it is necessary to find which of the various interface reactions is rate-controlling. An examination of Fassell's curves shows that $\theta \cong 0.2$ at 50 mm Hg at 550°C ; at 200 mm at 600°C ; and at 300 mm Hg at 625°C . At 655°C and above $\theta < 0.2$ for $p < 760$ mm Hg. For pressures below these values therefore the surface concentration of oxygen is approximately equal to the atmospheric concentration, and thus the pressure dependence of the oxidation rate is the same as the surface concentration dependence of the interface reaction. The linear rate-constant k is given at these low pressures by

$$K = K'p^n$$

where K' is independent of pressure. Thus if the logarithm of the oxidation rate is plotted versus the logarithm of the oxygen pressure the curve shows the following features

- (1) An initial period when the oxidation starts associated with the establishment of steady state. The form of this initial section cannot be predicted.
- (2) At high pressures the rate is independent of pressure, and the graph is rectilinear and parallel to the pressure axis.
- (3) As the pressure falls the rate will begin to show a pressure dependence.
- (4) Finally at low pressures the graph again becomes rectilinear, with slope of n .

EXPERIMENTAL METHOD

The values calculated above from FASSELL's curves for the pressures below which the reaction rate pressure dependence is equal to that of the rate-controlling step indicate that the value of n can be determined above 550°C using a Sievert's method in which the oxygen absorbed by the specimen is measured as a pressure drop in a constant reaction volume. The apparatus and its use to determine the pressure dependence of oxidation reactions have been described elsewhere^{9,10}. The reaction vessel is quartz, and because there was some evidence of reaction between the specimen and the quartz, the specimen is stood on a mullite pedestal. The specimens were cut from 0.5 mm sheet and had a geometrical surface area of about 4 cm². The edges were filed square in a hardened steel jig and ground to 4/0. The specimens were oxidised in the as-rolled condition. X-ray measurements with CuK α radiation were carried out on the scale and metal using both a Jones camera and a Philips Geiger-Müller spectrometer.

RESULTS

At 1,000°C the specimen burnt on the admission of oxygen, and at 500°C the rate is too slow to be measured with the present technique. The pressure dependence has been examined at five temperatures, 610°, 660°, 710°, 760° and 860°C. The results are plotted as log rate versus log pressure in Figs. 1 and 2. The curves have been displaced laterally and vertically by multiples of 10 for clarity. The best straight line is drawn through the low pressure points, and the value of n calculated from the slope is given at the top of the line.

The curves at 610°C (Fig. 1) have the expected shape. An initial period is followed by a vertical straight line indicating a pressure-independent region. The rate then shows an increasing pressure dependence until a straight line is established with a value of $n \simeq 0.5$. This line is established below 350 mm pressure, in good agreement with the value estimated above from FASSELL's curves. When the reaction had absorbed the original oxygen, a second volume was added, the pressure rising again to over 700 mm Hg. The curves show no initial period, but again show that the reaction is independent of pressure at high pressures.

At 660°C (Fig. 1) when it is expected that the surface concentration will be approximately equal to that of the atmosphere at all pressures below 760 mm, there is a short initial period followed by a straight line giving $n \simeq 1$. At about 350 mm Hg the curve changes to a second straight line with $n \simeq 0.5$.

At 710° and 760°C (Fig. 2) a straight line giving $n \simeq 0.5$ is established after a short

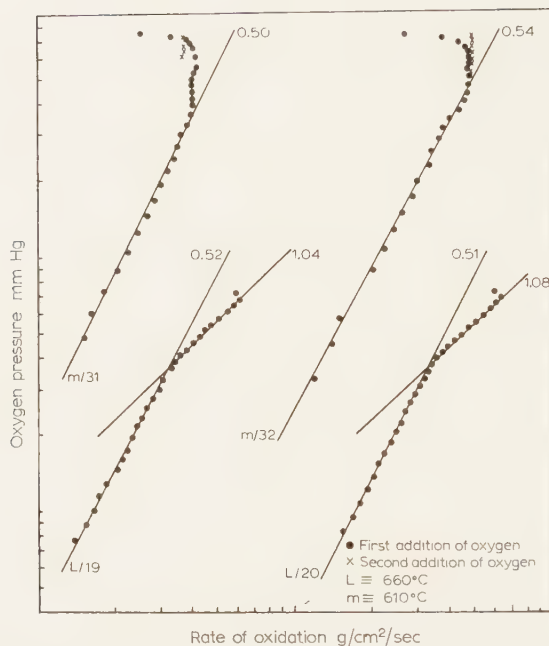


Fig. 1. The effect of oxygen pressure on the linear rate constant in the oxidation of tantalum at 610° and 660°C. The curves have been displaced laterally and vertically for clarity.

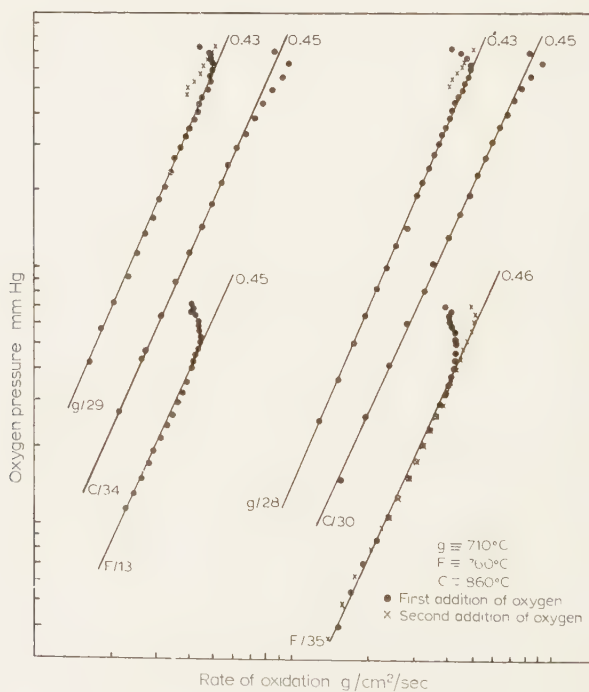


Fig. 2. The effect of oxygen pressure on the linear rate constant in the oxidation of tantalum at 710°, 760° and 860°C.

initial period, during which the curves have a vertical portion suggesting a pressure-dependent region. This is a transient effect produced during the approach to steady state, as is demonstrated by the behaviour on admitting a second volume of oxygen when the first had been practically exhausted by the reaction. In contrast to the similar curves at 610°C (Fig. 1) the graph has a slope corresponding to $n \simeq 0.5$ immediately the second admission is made.

At 860°C (Fig. 2) the graphs are straight lines giving $n \simeq 0.5$ after a very short initial period.

The change in pressure dependence at 660°C has been examined in more detail (Fig. 3). In the first runs (Fig. 1) the slope changed at a pressure of 350 mm, but in

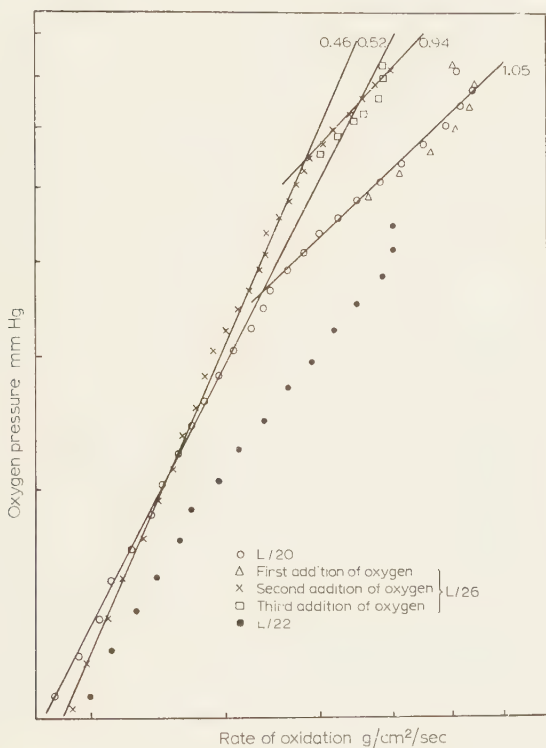


Fig. 3. The effect of oxygen pressure on the linear rate constant in the oxidation of tantalum at 660°C.

In each case this also corresponded to the same scale thickness. On cooling, the scale separated into two distinct layers. The weight of the outer layer approximately corresponded to the weight of scale formed at the point where the pressure dependence altered, as shown in Table I. Runs were then performed in which a second admission of oxygen was made when the pressure had fallen to only 500 mm Hg after the first addition. A typical curve is shown in Fig. 3. The rate depended linearly on the pressure for the first addition, and initially for the second addition; but when the pressure dropped to 550 mm after the second addition n altered to 0.5. The total thickness of the oxide was rather greater at this point than that at the break in the first runs.

The scales again showed two distinct layers. The pressure was allowed to fall to low values, and a third admission of oxygen made. The rate once again showed a linear dependence on pressure. Finally, a run was performed (shown in Fig. 3) in which the original pressure was 450 mm Hg. The initial slope of the graph corresponded to a value of n between 0.5 and 1 and decreased slowly to $n = 0.5$ as the pressure fell. In this case, the scale consisted of a single layer. From these results it appears that the change in pressure dependence is not simply a function of either pressure or scale thickness.

TABLE I

THE THICKNESS OF THE OUTER OXIDE LAYER ON TANTALUM AND ITS RELATION TO THE CHANGE IN SLOPE OF THE PRESSURE/RATE CURVES

No.	Temp.	Scale thickness at break — from Sievert's apparatus results	Weight of outer layer of scale	Pressure at break
		°C mg Ta ₂ O ₅ /cm ²	mg Ta ₂ O ₅ /cm ²	mm Hg
1 19	670	77.3	68.6	370
1 21	665	88.4	64.1	360
1 26	665	97.2	87.2	550
m 25	625	—	47.8	520*
m 31	620	—	64.6	450*
m 32	630	—	48.1	505*

* calculated from thickness of outer layer.

Since, at subatmospheric pressures, the linear surface concentration dependent process appears at 660°C but not at 710°C, it would be expected at 610°C. The scales at 610°C do show two distinct layers, and the weight of the outer layer shows that the change in reaction behaviour occurs at a point where the surface concentration is independent of pressure. Consequently, the change in the reaction is not reflected in the rate versus pressure curves. The scales at 710°C do not show a two-layer structure.

The layers of the scales were examined with X-rays. All were Ta₂O₅. The spacings corresponded more closely to those reported by VERMILYEA¹¹ than to those of HAHN¹². Additional faint lines were obtained at d spacings of 2.82, 2.1 and 2.02 Å. There was

TABLE II

RELATIVE INTENSITIES OF SOME IMPORTANT LINES IN Ta₂O₅

Line	Results from the literature			This investigation	
	dA	HAHN ¹²	VERMILYEA ¹⁰	FASSELL	max. min.
3.88	100	S	M	16	2
3.16	100	S	S	100	100
2.45	100	S	M	60	10
1.83	60	M	M	100	20
1.65	60	S	W	35	10

S = strong; M = medium; W = weak.

difference in structure or spacing between the inner surface of the inner scale and inner surface of the outer scale, although in all the specimens the outer surface of the outer scale had a very slightly larger spacing. The intensities of the lines differed considerably from those reported by HAHN and by VERMILYEA, indicating a preferred orientation in the scale. This is shown in Table II, which compares the intensities reported in the literature with the range of values found in this investigation for five important lines. The tantalum metal exhibited a preferred orientation due to cold-rolling, so it seems probable that the preferred orientation in the scale is due to an epitaxial relationship between the growing scale and the metal, suggesting that the scale forms coherently and then detaches. Each scale layer was composed of laminations, as reported by GEBHARDT AND SEGHEZZI⁷ and by BAKISH¹³.

DISCUSSION

At sufficiently low pressures, the oxidation rate depends on the square root of the pressure at all temperatures studied. Possible reactions in the process which can show pressure dependence of this type are the dissociation of the oxygen molecules, or the solution of oxygen in the metal, although it has been reported that the solution of oxygen in tantalum does not obey Sievert's law⁸. No diffusion process through a thick semiconductor oxide or gaseous diffusion through a porous oxide can give square root pressure dependence. It seems likely therefore that the dissociation of adsorbed molecules to atoms is slow compared with the adsorption process, but rapid compared with the incorporation of the separate atoms into the anion lattice of the oxide. The migration of the mobile species across the Ta_2O_5 scale and the reactions at the metal/oxide interface are rapid compared with the incorporation step. This model results in a linear rate dependent on the square root of pressure (*cf.* FASSELL, FASSTONE, LAIDLER AND EYRING¹⁴). The scale grows coherently until the internal shear stresses cause it to detach, when the coherent growth is repeated on the freshly exposed metal surface, producing a finely laminated scale.

At low temperatures, or at relatively high surface concentrations, the dissociation of the molecules of oxygen becomes more difficult. Eventually, the rate of dissociation of the adsorbed molecules becomes slow compared with the rate at which the dissociated atoms are incorporated into the lattice. This model results in a linear rate with a linear pressure dependence.

Using this model it is possible to explain most of the observed features of the oxidation.

CONCLUSIONS

The pressure dependence of the oxidation of tantalum has been studied in the temperature range 600°–860°C and the pressure range 1–760 mm Hg. The results confirm the view of FASSELL that the rate-controlling step is preceded by an equilibrium adsorption process. At sufficiently low pressures, the rate depends on the square root of the oxygen pressure, suggesting that the adsorbed molecules dissociate rapidly to oxygen atoms which are then incorporated in the anion lattice, this being the slow step. At lower temperatures and higher pressures the rate depends linearly on pressure, suggesting that the dissociation becomes slow compared to the incorporation step. The scale found on all specimens is Ta_2O_5 with a heavily preferred orientation suggesting coherent growth of the scale on a textured metal surface.

ACKNOWLEDGEMENTS

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IV. Mechanical Properties

DEFORMATION, FRACTURE, AND RADIATION DAMAGE, IN BODY-CENTRED CUBIC TRANSITION METALS

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SUMMARY

Recent advances in the dislocation theory of the deformation and fracture of body-centred cubic transition metals are reviewed. The theory is still largely phenomenological and is formulated in terms of the parameters σ_i and k_y in the empirical relation $\sigma_y = \sigma_i + k_y d^{-\frac{1}{2}}$ between yield stress and grain diameter. The application of the theory to body-centred cubic transition metals other than iron and steel has been hindered by the absence of reliable values of σ_i and k_y . Recent values obtained for molybdenum and niobium explain why the ductile-brittle transition temperature of molybdenum is much higher than that of niobium.

Experiments on the recovery of the electrical resistivity of deformed niobium, molybdenum, tantalum, and tungsten wires have shown that point defects, believed to be lattice vacancies, are created during deformation near room temperature. The activation energies for the diffusion of the vacancies are 1.0, 1.3, 1.35, and 1.7 eV, for niobium, molybdenum, tantalum, and tungsten, respectively.

Similar measurements have been made on neutron-irradiated niobium, molybdenum and tungsten. The results obtained agree well with those of the deformation experiments. It has been shown that the annealing of vacancies in irradiated niobium and molybdenum is accompanied by an increase in yield stress.

INTRODUCTION

During the past decade there has been a growing demand for body-centred cubic transition metals for special applications in the technologies of nuclear power, aeronautics, and space research. New preparation and fabrication techniques have been developed to meet this demand and the improved materials obtained by them have provided a stimulus to fundamental research into deformation and fracture. The purpose of this paper is to review some of this recent research and to discuss the results of it in terms of lattice defect theory.

The work to be considered falls into three categories:

(i) Experiments in which the tensile properties of a metal are measured as a function of grain size at constant temperature. These give information about the lattice friction stress of the metal and about the interaction between dislocations and their impurity atmospheres.

(ii) Experiments in which the annealing kinetics of point defects are studied by following the thermal recovery of the electrical resistivity of deformed wire specimens.

These provide values of the activation energies for the diffusion of the defects. The results can be compared with those of similar experiments on point defects in neutron-irradiated specimens.

(iii) Experiments in which point defects created during irradiation interact with dislocations to produce a change in the mechanical properties of the metal.

The description of these experiments will be prefaced, in the next section, by an outline of the present state of the dislocation theory of deformation and fracture as applied to this group of metals.

THEORY OF DEFORMATION AND FRACTURE

All of the body-centred cubic transition metals except tantalum have been shown to undergo a transition from ductile to brittle behaviour as the temperature is lowered. The effect seems to be closely related to a rapid increase in yield stress with decreasing temperature which precedes the onset of brittleness and occurs in a temperature range characteristic of each metal. A partial understanding of this strong temperature dependence of yield stress for the case of mild steel has been achieved by HESLOP AND PETCH¹, who measured the temperature dependence of the two parameters σ_i and k_y in the relation

$$\sigma_y = \sigma_i + k_y d^{-\frac{1}{2}} \quad (1)$$

between lower yield (shear) stress, σ_y , and grain diameter, $2d$. Their results showed that the biggest contribution to the temperature dependence of the yield stress comes from σ_i and that this contribution is independent of the impurity content. An interpretation of σ_i and k_y in terms of dislocation theory can be developed using a model of yield propagation suggested by COTTRELL² and others.

It is believed that the propagation of a Lüders band at the lower yield stress proceeds by the operation of Frank-Read sources in unyielded grains by the stress fields of dislocations piled-up against the grain boundaries in yielded grains. The dependence of lower yield stress on grain diameter according to this model can be found by using the expression

$$\sigma = \sigma_a [1 + (d/x)^{\frac{1}{2}}] \quad (2)$$

derived by ESHELBY, FRANK AND NABARRO³ for the shear stress, σ , at a moderate distance, x , ahead of a pile-up formed under an applied shear stress, σ_a . If l^* is the average distance from a grain boundary to the nearest dislocation source, and σ_a is the stress required to tear the dislocation line in the source away from its impurity atmosphere, then

$$\sigma_a = \sigma_y [1 + (d/l^*)^{\frac{1}{2}}] \quad (3)$$

Rearranging eqn. (3), and assuming that $l^* \ll d$, the dependence of yield stress on grain diameter is

$$\sigma_y = \sigma_a l^*^{\frac{1}{2}} d^{-\frac{1}{2}} \quad (4)$$

Equation (4) does not agree with the experimental relation, eqn. (1), but can be made to do so by supposing that a lattice friction stress, σ_i , acts on each dislocation in

position to the applied stress. Both COTTRELL and HESLOP AND PETCH attribute the temperature-dependent part of this friction stress to the Peierls-Nabarro stress of the lattice. Comparing eqns. (1) and (4) we have also

$$k_y = \sigma_d l^{* \frac{1}{2}} \quad (5)$$

which shows that k_y is a measure of the strength of the dislocation locking, but also depends on l^* , which is probably determined by the scale of the Frank-Read network in the metal.

Below the ductile-brittle transition temperature PETCH⁴ found that the brittle fracture stress varied with grain size according to the relation

$$\sigma_f = \sigma_i + k_f d^{-\frac{1}{2}} \quad (6)$$

The similarity between this equation and eqn. (1) suggests that at low temperatures, where yield propagation is inhibited by strong dislocation locking, pile-ups provide the stress concentration necessary to initiate fracture. A theory of brittle fracture based on this idea has been worked out by STROH⁵. STROH considered two mechanisms whereby a pile-up can initiate fracture. In the first the leading dislocations in the pile-up are pushed together until they coalesce to nucleate a crack. In the second a crack is nucleated in the region of high tensile stress ahead of the pile-up. STROH's calculations show that about the same applied stress is required for either of these mechanisms and that as soon as the crack is nucleated it will propagate to cause fracture. The theory correctly predicts the grain size dependence of fracture stress, eqn. (6), and several other effects, but does not readily predict the increase in transition temperature which is observed when either the grain size or lattice friction stress is increased.

At about the same time (1957) both PETCH⁶ and COTTRELL⁷ realised that these two effects not predicted by STROH's theory could be explained by assuming that the stress required to propagate a crack is greater than that required for its nucleation. This is contrary to the result obtained by STROH but can be explained by supposing that the propagation of the crack is prevented by the plastic deformation accompanying its growth, an effect not included in STROH's theory. The quantitative theory developed by COTTRELL was based on the nucleation of a crack by the coalescence of dislocations. He suggested a mechanism involving the coalescence of dislocations from intersecting slip bands whereby the crack could be nucleated at a lower stress than that required for STROH's mechanism, but the results he obtained do not depend on which of the two mechanisms actually operates. The conditions for the propagation of a crack during a tensile test are

$$\left. \begin{aligned} (\sigma_i d^{\frac{1}{2}} + k_y) k_y &\geq \beta \mu \gamma \\ \sigma_y k_y d^{\frac{1}{2}} &\geq \beta \mu \gamma \end{aligned} \right\} \quad (7)$$

where β is a constant which is nearly unity, μ the rigidity modulus, and γ the effective surface energy for fracture. Above the ductile-brittle transition temperature the propagation stress is greater than the yield stress, but if it is reached during strain-

hardening at a (shear) stress σ_f' , then

$$\sigma_f' = \frac{\beta\mu\gamma}{k_y} \cdot d^{-\frac{1}{2}} \quad (8)$$

Below the ductile-brittle transition temperature the brittle fracture (shear) stress is given by

$$\sigma_f(\sigma_f - \sigma_i)d = \beta\mu\gamma \quad (9)$$

The brittle fracture criterion, eqn. (7), now includes the grain size and lattice friction stress and predicts about the right dependence of transition temperature on them. The conditions under which eqn. (8) apply correspond to ductile cleavage fracture, and the only set of results available, those of Low⁸ on steel, are in reasonable agreement with it. The form of eqn. (9) is different from that derived empirically from experiment, but over the ranges of grain size and temperature so far studied is practically identical to it. The value of γ required to make eqns. (7)–(9) agree with the experimental results on iron is about five to ten times the theoretical value.

COTTRELL's theory is largely phenomenological and before it can be applied to a given metal σ_i , k_y and their temperature dependence must be measured for it. Until recently, these measurements had only been carried out for iron and steel, but now values for niobium and molybdenum have been obtained. These results, which explain why niobium has a much lower transition temperature than molybdenum, will be discussed in the next section.

DEFORMATION AND FRACTURE OF NIOBIUM AND MOLYBDENUM

Three sets of measurements have been reported in which σ_i and k_y were measured for niobium at room temperature, 195°K, and 77°K. CHURCHMAN⁹ found that, for a strain rate of $3.3\text{--}8.3 \cdot 10^{-4} \text{ sec}^{-1}$, σ_i increased from 9 to 34 kg/mm² over this temperature range, and that k_y was about $3\text{--}5 \cdot 10^6 \text{ dyne cm}^{-3/2}$. At 77°K the specimens with the largest grain size were brittle. Using material that had been outgassed by electron bombardment, ADAMS, ROBERTS AND SMALLMAN¹⁰ observed an increase in σ_i from 7 to 34 kg mm^{−2} over the same temperature range for a strain rate of $2.02 \cdot 10^{-4} \text{ sec}^{-1}$. Their values of k_y varied from $2.76 \cdot 10^6 \text{ dyne cm}^{-3/2}$ at room temperature to $5.18 \cdot 10^6 \text{ dyne cm}^{-3/2}$ at 77°K. At the latter temperature none of their specimens were brittle, but on increasing the strain rate to $6.18 \cdot 10^{-2} \text{ sec}^{-1}$ specimens with the coarsest grain size became brittle and σ_i and k_y increased to 39 kg mm^{−2} and $7.25 \cdot 10^6 \text{ dyne cm}^{-3/2}$ respectively. At 20°K coarse-grained specimens were brittle at the lower strain rate. Values of σ_i and k_y were not obtained at this temperature because mechanical twinning was observed and its effect on the initiation of yielding is not yet understood. Using material of somewhat higher purity than that of ADAMS *et al.* and a strain rate of $0.88 \cdot 10^{-4} \text{ sec}^{-1}$, JOHNSON¹¹ observed an increase in σ_i from 9 to 36 kg mm^{−2} between room temperature and 77°K but no dependence of yield stress on grain size, *i.e.* k_y was zero. Because k_y was zero the shape of the load–elongation curve was independent of grain size and in this respect this set of results differs strikingly from the other two. At 20°K twinning was observed but the shape of the load–elongation curve was still independent of grain size. Typical load–elongation curves obtained at room temperature, 195°K, and 77°K, and the yield stress values obtained at these temperatures, are shown in Figs. 1 and 2, respectively. The values of σ_i and k_y from all three sets of

periments are included in Table I. The analysis figures quoted in Table I for the niobium used by CHURCHMAN AND ADAMS *et al.* are nominal, except that CHURCHMAN estimated the oxygen content of his material from its hardness. The figures for non-metallic impurities in JOHNSON'S niobium are also nominal, but the figures for oxygen and nitrogen were obtained by the analysis of fractured specimens.

The only measurements reported for molybdenum are those of JOHNSON¹² carried out at room temperature at a strain rate of $0.88 \cdot 10^{-4} \text{ sec}^{-1}$. The values of σ_i and k_y

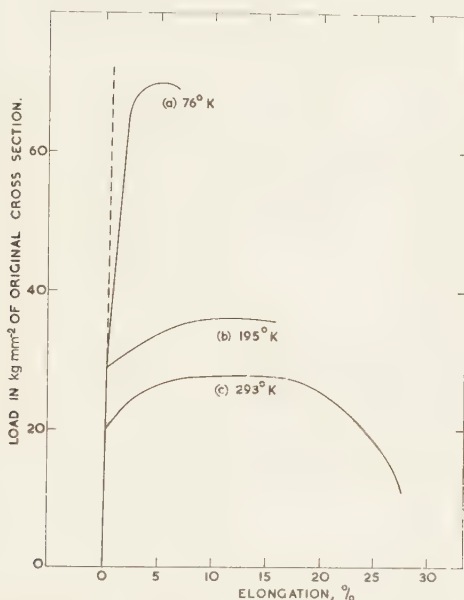


Fig. 1. Load-elongation curves for niobium specimens tested at 77° , 195° and 293°K (after JOHNSON¹¹, reproduced by courtesy of *Acta Met.*).

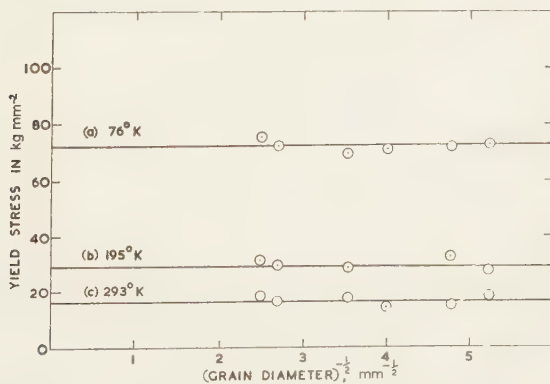


Fig. 2. The effect of grain size on the tensile yield stress of niobium at 77° , 195° and 293°K (after JOHNSON¹¹, reproduced by courtesy of *Acta Met.*).

VALUES OF σ , k_y , AND			
Metal	Principal impurities	Temp. (°K)	Strain (sec ⁻¹)
Niobium	0.04-0.05% O ₂ , 0.1% Ta, 0.01% Ti, Co, Si and N ₂ .	77°	3.3-8.3
		195°	
		293°	
Niobium	0.3% Ta, 0.3% Fe, 0.15% Si, 0.07% C, 0.05% N ₂ , 0.02% H ₂ , 0.01% O ₂ .	77°	2.02-10
		195°	
		293°	6.18-
		77°	
Niobium	0.3% Ta, 0.05% Ti, 0.03% Fe, 0.03% O ₂ , 0.01% N ₂ .	77°	0.88-
		195°	
		293°	
Molybdenum	0.01% Fe, 0.008% C, 0.003% N ₂ , 0.002% Si, 0.001% O ₂ .	293°	0.88-



Fig. 3. The effect of grain size on the load-elongation curve of molybdenum at room temperature (after JOHNSON¹², reproduced by courtesy of *Phil. Mag.*).

obtained (Table I) were 5.5 kg mm⁻² and 6.0·10⁷ dyne cm^{-3/2} respectively. All the specimens in this experiment were ductile, but the mode of fracture changed from

MOLYBDENUM

k_y ($\text{dyne cm}^{-3/2}$)	γ' (ergs cm^{-2})	Authors	Ref.
3-5·10 ⁶	—	CHURCHMAN (1960)	9
5.18·10 ⁶	13,600	ADAMS <i>et al.</i> (1959)	10
3.8·10 ⁶			
2.76·10 ⁶			
7.25·10 ⁶	—	JOHNSON (1960)	11
zero			
zero			
zero	12,000	JOHNSON (1959)	12
6.0·10 ⁷			

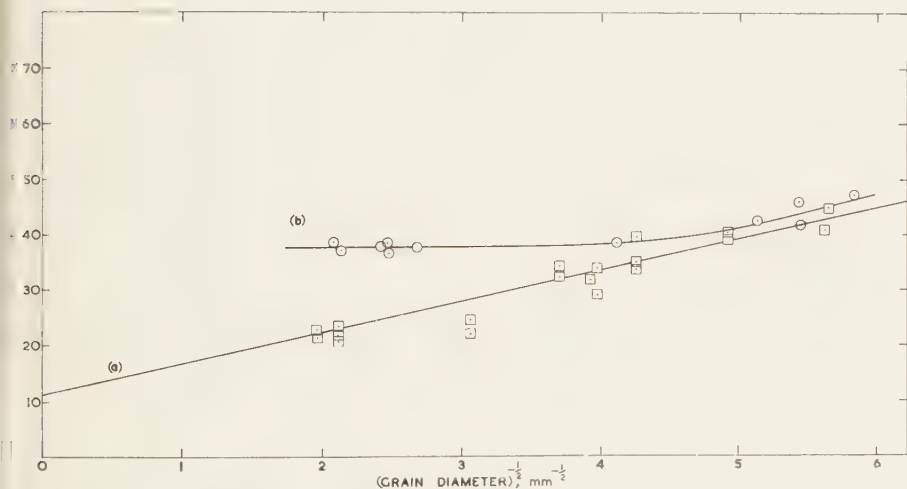


Fig. 4. The effect of grain size on the tensile yield stress of molybdenum, (a) before irradiation and, (b) after irradiation to a dose of $2 \cdot 10^{19}$ n.v.t. (after JOHNSON²⁵, reproduced by courtesy of *Phil. Mag.*).

brous to cleavage as the grain size increased. Typical load-elongation curves for three different grain sizes, and the yield stress results plotted as a function of $d^{-1/2}$, are shown in Figs. 3 and 4a, respectively.

The measurements made by ADAMS *et al.* on the effect of strain rate on σ_s and k_y show that it is small enough to be neglected in comparing the three sets of results on molybdenum.

The values of k_y obtained by both CHURCHMAN AND ADAMS *et al.* are more than ten times smaller than those for iron at similar temperatures. Assuming that l^* is about the same for niobium as for iron this means, from eqn. (5), that the dislocation sources in niobium are correspondingly less strongly locked than those in iron. The results of ADAMS *et al.* show that, as for iron, the strength of the locking increases with decreasing temperature. JOHNSON's results for k_y imply that in his material the dislocation locking was negligible. Another feature common to iron, which is also shown by these three sets of results, is the rapid increase in lattice friction stress with decreasing temperature.

The value of γ calculated by ADAMS *et al.* from the values of σ_i , k_y and d at the onset of brittleness in their specimens was, using eqn. (7), $13,600 \pm 15\%$ ergs cm⁻². This is about five times the theoretical value of the surface energy and is therefore in line with the values of γ obtained for iron by the same method. Because the values of γ for iron and niobium are comparable, and k_y is much larger for iron than for niobium, a much higher value of σ_i , *i.e.* a lower temperature, is required to satisfy the brittle fracture criterion, eqn. (7). This means that the low ductile-brittle transition temperature of niobium is a direct consequence of the weak locking of its dislocation sources. In the case of JOHNSON's experiments, where k_y was zero, the brittle fracture criterion cannot be satisfied at any temperature; this explains why the material was never completely brittle.

The value of k_y for molybdenum at room temperature is nearly twice that for iron and more than twenty times that for niobium. This implies that the dislocation sources in molybdenum are very strongly locked by their impurity atmospheres. The value of σ_i is rather lower than for niobium, but this may be partly due to the higher purity of the molybdenum. JOHNSON calculated a value of γ from the stress for cleavage fracture of his coarse grained specimens using eqn. (8). The value he obtained was 12,000 ergs cm⁻², which is about six times the theoretical value and therefore in agreement with the results obtained for iron and niobium. Preliminary results of experiments in which JOHNSON's work has been extended to lower temperatures¹³ have shown that both σ_i and k_y increase with decreasing temperature down to the ductile-brittle transition temperature, which is about 190°K. Using an argument similar to that applied to niobium, it is apparent that this high ductile-brittle transition temperature is a result of particularly strong dislocation locking.

POINT DEFECTS IN NIOBIUM, MOLYBDENUM, TANTALUM AND TUNGSTEN

The theories and experimental results dealt with in the preceding two sections were concerned mainly with brittle fracture and the initial stages of deformation. The theory of strain-hardening in body centred cubic metals has received less attention, partly because of the inherent complexity of the dislocation mechanisms involved, and partly because the occurrence of the yield point and Lüders strain effects make it impossible to study hardening for small strains. One aspect of the subject which has been studied recently is the creation of point defects during deformation.

The experiments are usually carried out on a wire specimen which has been deformed in tension or by cold drawing. On annealing at a suitably high temperature the point defects become mobile and diffuse through the lattice until they are annihilated at dislocations, grain boundaries, and free surfaces. Their annihilation is

followed by interrupting the annealing treatment to make electrical resistivity measurements on the specimen at the temperature of liquid nitrogen, hydrogen, or helium. Two types of experiment are usually carried out. In the first, the temperature range in which the recovery occurs at a convenient rate is established by plotting an isochronal annealing curve. To do this the resistivity of the specimen is measured between annealing treatments carried out for a constant time at a series of successively higher temperatures. Part of an isochronal curve for a tantalum wire strained 14% in tension is shown in Fig. 5. The period of each anneal was four hours. In the second, the activation energy associated with the recovery process is determined by plotting an isothermal recovery curve for a temperature T_1 and then continuing it after the



Fig. 5. Part of an isochronal annealing curve for a tantalum wire specimen strained 14% in tension showing the recovery of the electrical resistivity during the annihilation of vacancies. The period of each anneal was four hours.

temperature has been raised to T_2 . If $(dR/dt)_1$ and $(dR/dt)_2$ are the time rates of change of resistance for the temperatures T_1 and T_2 respectively at the point of intersection of the curves, the activation energy, ΔH , can be calculated from the relation

$$\log_e \frac{(dR/dt)_1}{(dR/dt)_2} = -\frac{\Delta H}{k} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (10)$$

where k is Boltzmann's constant. Another method of measuring ΔH adopted by some workers involved measuring the time, t , taken to reach a given stage in the

recovery, as a function of the annealing temperature, in a series of isothermal anneals. In this case, provided the recovery is exponential with time, the activation energy is obtained from the relation

$$\log_e t = A + \frac{AH}{kT} \quad (11)$$

by plotting $\log_e t$ as a function of $1/T$. All the available results obtained from these two types of experiment are listed in Table II. The results of similar experiments on point defects introduced by neutron irradiation are included for comparison.

In the experiments of KINCHIN AND THOMPSON and THOMPSON the irradiations were carried out at the temperature of liquid nitrogen or helium. THOMPSON distinguishes four stages in the recovery of irradiated tungsten, the first below -170°C , the second between -170° and 350°C with an activation energy rising from 0.25 to 1.7 eV, the third between 350° and 450°C with an activation energy of 1.7 eV, and the fourth above 450°C . By analogy with the behaviour of the face-centred cubic metals, in which the properties of point defects are rather better understood, THOMPSON attributes the first three of these four stages to the annihilation of interstitials, trapped interstitials, and vacancies, respectively. The vacancy stage is therefore the one listed in Table II. NEIMARK AND SWALIN observed an additional recovery stage

TABLE II
THE ANNEALING KINETICS OF VACANCIES IN NIOBIUM, MOLYBDENUM, TANTALUM AND TUNGSTEN

<i>Metal</i>	<i>Melting point</i>	<i>Type of expt.</i>	<i>Temperature range</i>	<i>Activation energy</i>	<i>Authors</i>	<i>Ref.</i>
Niobium	2,468°C	Deformation	80°–120°C	1.0 eV	PEACOCK AND JOHNSON (1960)	14
		Irradiation	80°–120°C	1.0 eV	PEACOCK AND JOHNSON (1960)	
Molybdenum	2,622°C	Deformation	~ 150°C	1.26 eV	MARTIN (1956)	15
		Irradiation	~ 150°C	1.3 eV	KINCHIN AND THOMPSON (1958)	16, 17
			~ 150°C	1.3 eV	PEACOCK AND JOHNSON (1960)	14
Tantalum	2,996°C	Deformation	80°–140°C	1.35 eV	READ AND JOHNSON (1958)	18
Tungsten	3,370°C	Deformation	300°–400°C	1.73 eV	SCHULTZ (1959)	19
			325°–450°C	1.7 eV	NEIMARK AND SWALIN (1960)	20
		Irradiation	~ 320°C	1.7 eV	KINCHIN AND THOMPSON (1958)	17
			350°–450°C	1.7 eV	THOMPSON (1959)	21

in tungsten which had an activation energy of 1.5 eV. This they tentatively attributed to the annihilation of di-vacancies.

The excellent agreement between the results listed in Table II leaves no doubt that deformation and neutron irradiation produce the same species of defect in a given metal. The systematic increase of activation energy with the melting point of the

metal suggests that the defects are of the same species in all four metals. It therefore seems reasonably safe to assume that all the recovery processes listed in Table II were due to the annihilation of vacancies.

RADIATION HARDENING AND EMBRITTLEMENT OF NIOBIUM AND MOLYBDENUM

It is now well established that neutron irradiation increases the ductile-brittle transition temperature of iron and steel. The effect has also been observed with molybdenum^{22,23} and tungsten²². HULL AND MOGFORD²⁴ attempted to elucidate the mechanism of this embrittlement in EN2 steel by studying the effect of irradiation on σ_i and k_y . They found that σ_i increased and attributed the effect to the interaction of moving slip dislocations with the stress fields of point defects or groups of defects created during irradiation. For this special case of σ_i varying and k_y constant the brittle fracture criterion, eqn (8), becomes

$$\sigma_i d_c^{\frac{1}{2}} = \text{a constant} \quad (12)$$

where d_c is the critical grain size for brittle fracture. This result was verified by HULL AND MOGFORD. In applying the same approach to the embrittlement of molybdenum, JOHNSON²⁵ found that an irradiation dose of $2 \cdot 10^{19}$ n.v.t. made about half the specimens of all grain sizes brittle and increased the yield stresses of the remainder in a way that depended on their grain size (Fig. 4b). In attempting to interpret these results JOHNSON suggested that in molybdenum, where the dislocations are not enclosed in a precipitate, as in steel, the dislocation structure of the metal is modified by climb processes caused by the point defects created during irradiation.

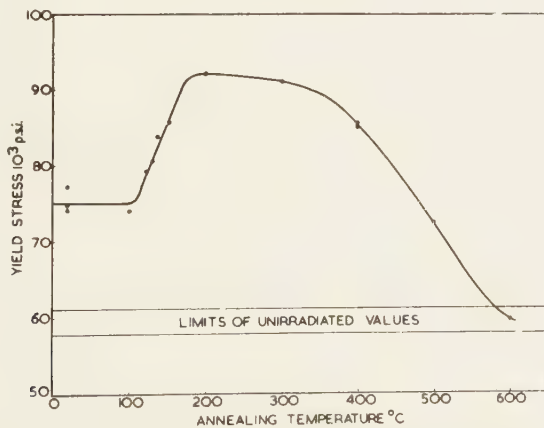


Fig. 6. An isochronal annealing curve for niobium showing the increase in yield stress accompanying the annihilation of vacancies. The period of each anneal was one hour (after MAKIN AND MINTER²⁶, reproduced by courtesy of *Acta Met.*).

Evidence that some type of interaction between vacancies and dislocations occurs when the vacancies are annihilated by annealing has been obtained for molybdenum by MAKIN AND GILLIES²² and for niobium by MAKIN AND MINTER²⁶, but the nature of this interaction is not yet understood. In both cases the annihilation of the vacan-

cies was accompanied by an increase in yield stress and the appearance of a yield point. The yield stress results obtained by MAKIN AND MINTER are reproduced in Fig. 6.

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MECHANICAL PROPERTIES ATTAINABLE BY ALLOYING OF REFRACTORY METALS

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SUMMARY

This paper discusses the status of mechanical properties of W, Mo, Ta and Nb-base alloys as of April 1960. Basic metallurgical considerations with respect to high temperature strength, ductility and transition temperature are covered. The mechanical properties at elevated temperatures attainable by both artificial dispersoid systems and regular alloy systems are presented and discussed from the standpoint of dispersion, solid solution and strain hardening. On the basis of elevated temperature strength, the order of decreasing superiority is W, Mo, Ta, and Nb-base alloys; whereas on the basis of strength-weight ratio, this order is Mo, W, Nb, and Ta-base alloys.

INTRODUCTION

On the basis of high melting point and commercial availability, the so-called "big-four" refractory metals (W, Ta, Mo and Nb) are considered to be most promising for structural applications at super high temperatures. A considerable amount of research and development has been carried out in recent years to improve the mechanical properties of these four metals by alloying. Because of the demands of the space age, the tempo of such activities is constantly being increased. It is the main purpose of this paper to assess the present status of alloys based on the "big-four" refractory metals from the standpoint of high temperature strength.

For elevated temperature applications, the mechanical properties that are generally considered of prime importance are high tensile strength and high rupture strength. In surveying the available elevated temperature mechanical property data pertaining to alloys based on the "big-four" metals, it was found that most of the effort has been concentrated on tensile properties. Stress-rupture properties have received somewhat less attention; creep rate data are relatively scarce. In line with the purpose of this paper, it was decided to make comparisons on the basis of both tensile and stress-rupture strength at temperatures of 1,800°F (980°C) and higher.

From the standpoint of primary hot working operations on ingots and billets, high strength at elevated temperatures is a detriment. However, this disadvantage can be overcome by carrying out such operations at temperatures that are high enough

to result in sufficient softening. As an example, a special rolling mill and impact extruder has been constructed by the Universal Cyclops Steel Corporation. This equipment will operate up to least 3,630°F (2,000°C) in an argon-filled room.

For some of the alloy systems based on the "big-four" metals, a compromise between strength at the application temperature and plasticity at the primary working temperature may be required. In order to effect the best compromise possible the optimum alloy (and interstitial) content must be determined for a given alloy system. This will differ from the composition that results in maximum elevated temperature strength. The sacrifice in strength necessary is usually greater the lower the primary working temperature employed. Such methods as high speed deformation and the use of compressive stress (extrusion) during primary hot working operations require less of a sacrifice in strength.

With respect to secondary working operations, high strength is also more of a detriment the lower the fabricating temperature. However, such difficulties can usually be overcome by carrying out the deformation in a number of steps with appropriate stress relief or annealing treatments in between. The greater the plasticity and the lower the strength at the fabricating temperature, the more economical will be the secondary working operations.

It is not generally realized that ductility in the ambient temperature range is important even though fabrication is carried out at elevated temperatures. A part made from a refractory alloy will usually be subjected to heating and cooling cycles (either during fabrication or in service). Therefore, the alloy must be able to resist the thermal stresses that are developed. However, it is not usually possible to specify accurately the minimum ductility required for a given application. The magnitude and effects of thermal stresses are usually difficult to evaluate and only rough approximations can be made. For this reason, there has been a tendency to require a low transition temperature (preferably below room temperature) rather than a particular value of room temperature ductility.

There are various ways of compensating for low ductility or high transition temperature. Thus, slow heating and cooling rates can avoid high thermal stresses. Improved design can help by increasing support to critical sections and minimizing stress concentrations. Fastening of turbine buckets is an example of improved design.

It should be noted that the important refractory alloy applications differ markedly in ductility requirements. For example, alloys used for rocket nozzles usually require far less ductility than those used for turbine buckets. The ductility obtained in rocket nozzles will differ depending on whether they are made by slip casting, spinning or pressing and sintering. Other applications such as sheet metal components which include leading edges and panels for hypersonic vehicles have still different requirements.

In view of the above considerations, no attempt was made to compare refractory alloys on the basis of room temperature ductility. However, such information is listed in the tables of mechanical properties presented in this paper so that difficulties due to low ductility may be anticipated to some extent. In judging these data, it should be realized that ductility values vary with specimen size, shape, surface condition (roughness and contamination), test temperature and strain rate. Furthermore, a test specimen is generally not representative of an actual application because section size, shape and loading conditions can differ markedly from the test conditions.

BASIC METALLURGICAL CONSIDERATIONS

Factors affecting high temperature strength

Alloying results in increased high temperature strength by such phenomena as solid solution hardening, formation of a second phase, and increased resistance to both recrystallization and grain growth. The occurrence of a second phase as finely dispersed particles throughout the grains of the matrix (or as grain boundary films) can be very potent with respect to hardening. Alloying generally involves (effective combinations of) substitutional and interstitial elements. Substitutional atoms exert their influence by either solid solution hardening or by interaction with interstitial elements to form finely dispersed second phase particles. Thus far, alloys containing second phases based on substitutional elements only have proved too brittle to be even potentially useful in the vast majority of applications. Interstitial atoms can improve strength by solid solution hardening to varying extents; but their most effective use involves formation of finely dispersed second phase particles. Such particles act to increase strength by retardation of recrystallization and grain growth as well as by dispersion hardening.

The formation of what is commonly called dispersoid systems, *i.e.* alloys containing dispersed particles, may be classified as either "artificial" or "regular". Artificial dispersoids are generally made by powder metallurgy methods. Mixtures of powdered refractory metals and hard compounds such as oxides, carbides or nitrides can be pressed and sintered to form a dense alloy. The most extensive research and development work has been on dispersed oxides. Somewhat more attention has been paid to carbides than to nitrides. Artificial dispersoid systems are believed to exert their greatest effect on high temperature strength by retarding recrystallization and grain growth. Thus far, artificially dispersed particles cannot be made small enough to give strength to the degree possible with regular dispersoid systems.

Regular dispersoid systems involve the formation of finely dispersed second phase such as a carbide, oxide or nitride, usually after melting and fabrication. Thus far, carbide dispersion has been found to be more effective in conferring high temperature strength than an oxide or nitride. Finer carbide dispersions can be obtained in regular than in artificial systems, and, therefore, greater resistance to recrystallization and grain growth is obtained.

Information as to the conditions under which precipitation actually occurs in a given system is generally lacking. The rate and extent of precipitation is dependent on prior temperature-time-strain history as well as on chemical composition. The possibilities are that precipitation occurs (a) on cooling from the molten condition; (b) on reheating, straining, and cooling during fabrication; (c) on reheating after straining; and (d) on heating to, stressing at and cooling from the application temperature. If precipitates are already present before stressing at the application temperature occurs, they presumably contribute to elevated temperature strength if they resist coalescence to a marked extent. On the other hand, precipitation that occurs during stressing at the application temperature may contribute by the initial mechanism of precipitation hardening as well as by resistance to subsequent coalescence. Plastic deformation carried out below the recrystallization temperature (referred to as cold work, hot-cold work, or warm work), results in strain hardening. The degree of strain hardening for a given amount of plastic deformation is increased if alloying

elements which differ in atomic size from that of the matrix are present. Even small amounts of alloying elements (below 1%) can result in large strain-hardening effects. The increased strength due to working is usually maintained on heating above the temperature at which plastic deformation was carried out; however, there is a tendency for recrystallization temperature to be lower the greater the amount of plastic deformation. In many cases, this tendency can be overcome to a large degree if dispersed particles are present or form on reheating and/or stressing.

The use of what is called a stress relief treatment after working refractory metals and alloys is fairly common. This involves heating to a selected temperature below that of regular recrystallization and can be considered as a recovery treatment as well as a treatment for relief of macro-residual stresses. Although there are several processes involved in the recovery of metals and alloys, the one generally believed to increase strength is the formation of substructure. Sub-boundaries which form by the alignment of dislocations of like sign in a given location within a primary grain can increase strength and lower creep rate by offering resistance to movement of dislocations generated by subsequent external stressing. At the present time, there are some indications that substructure formations can result in increased strength in refractory metals. However, the effect appears to be relatively small.

Factors affecting ductility and transition temperature

Considered with respect to increasing room temperature ductility (or decreasing transition temperature), the order of the "big-four" refractory metals in the unalloyed condition is generally as follows: W, Mo, Nb and Ta. For a given metal, ductility decreases with higher interstitial content although Nb and Ta are less sensitive than W and Mo in this respect. With alloying, there is a tendency for a decrease in ductility that usually accompanies strengthening. This tendency is opposed by the solid solution purification effect associated with the ability of certain alloying elements to combine with interstitial elements and form second phases. A net increase or decrease in ductility results from alloying depending on the relative magnitudes of these tendencies. In the special case of Re as an alloying element for W or Mo, the observed increase in or maintenance of ductility level is considered to be due to a change in interfacial energy which prevents the occurrence of continuous oxide films at grain boundaries.

Straining the "big-four" refractory metals or their alloys above the transition temperature but below their recrystallization temperature (excluding the temperature range over which strain aging occurs) may prove beneficial to transition temperature in some cases. This improvement (which is orientation-dependent) is generally ascribed to the phenomenon of "fibreing" as manifested by elongation of grains in the direction of straining. An increase in transition temperature usually occurs with respect to stressing in the perpendicular directions. The lower transition temperature in the direction of straining may be due to (a) effective decrease in grain size as measured along the perpendicular direction, (b) occurrence of preferred orientation, (c) disruption of grain boundary films, and (d) rheotropic recovery due to freeing of dislocations from the pinning effect of interstitial atoms. Obviously, these mechanisms will vary in their effects depending on base metal, alloy content, interstitial content, and thermal-mechanical history.

PRESENTATION AND DISCUSSION OF MECHANICAL PROPERTY DATA

In the following sections on W, Ta, Mo and Nb base alloys, data on tensile properties (yield strength, tensile strength, elongation and reduction of area) and on 100-hour rupture strength are presented. The available room temperature tensile properties are given for all alloys. Tensile and stress rupture properties are given for 1,800°F (1,000°C) and above for Mo and Nb-base alloys, and 2,000°F (1,000°C) and above for Ta and W alloys. Typical room and elevated temperature data are given for unalloyed Ta, Mo and Nb metals in order that the effects of alloying can be better evaluated. The mechanical property data presented are discussed under the following headings: (a) properties of the unalloyed base metal, (b) artificial dispersoid systems, and (c) solid solution alloy systems. Some of the basic metallurgical considerations previously discussed are utilized in an attempt to describe the specific effects of alloying elements. The mechanical properties and the extent of improvement attainable by alloying of the base metal are summarized. Comparisons are made of the high temperature tensile and rupture strength of the best alloy for each base metal at selected temperatures taking into account density. Finally, the gaps in present knowledge and the need for further information are discussed.

TABLE I
MECHANICAL PROPERTIES OF W AND W-BASE ALLOYS

Ref.	Alloy	Condition*	Test temp. (°F)	Approx. Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El. %	R.A. %	100-hour R.S. k.s.i.
(1)	W	—R	2,000		34			22
(2)	"	"	2,200					19
(3)	"	PM-R	2,500		32			10
			3,000		19			
			3,500		11			
			4,000		9			
(1)	"	PM-W	2,000		59			
(3)	"	"	2,500		49			
			2,700		30			
			3,500		11			
(2)	2 ThO ₂	PM-W	2,500	41	42		74	20
			2,700	38	39		38	
	0.4 TaC	PM-W	2,500	56	67		42	
(4)	0.57 Nb	AC-W	3,000	50	60	20	82	
	0.88 Nb	"	3,000	45	46	15	85	
	"	"	3,500	7.5	18	31	98	
	0.07 Ti	"	3,000	14	17	36	98	
	"	"	3,500	8	13	37	98	
	0.12 Zr	"	3,000	41	48	16	39	
	"	"	3,500	11	15	49	98	
	"	"						
(5)	30 Re	AC-R	70		195	5		
	"	"	2,000		150	7		
	"	"	2,400		135	8		
	"	"	3,000		50	13		
	"	AC-W	70		310	6		
			2,000		170	7		
			2,400		80	8		
			3,000		30	9		

PM, powder metallurgy; AC, arc-cast; R, recrystallized; W, worked.

STATUS OF W ALLOYS

Unalloyed W metal

As shown in Table I, the tensile strength of unalloyed W decreases from 34 to 11 k.s.i. for the recrystallized condition and from 59 to 11 k.s.i. for the worked condition over the temperature range of 2,000 to 3,500°F (1,095 to 1,925°C). The rupture strength in the recrystallized condition is 22 and 10 k.s.i. for 2,000 and 2,500°F (1,095 and 1,375°C), respectively. These data are for unalloyed W of very low carbon and oxygen contents.

Artificial dispersoid systems

As compared with unalloyed W in worked condition, the addition of 2% ThO₂ to W by powder metallurgy is beneficial from the standpoint of tensile strength at 2,700°F (1,480°C), 39 vs. 30 k.s.i. At a lower temperature of 2,500°F (1,370°C), unalloyed W appears to be superior, 49 vs. 42 k.s.i. However, this may be due to a difference in the extent of working.

A W-0.4 TaC alloy has been found to possess the highest elevated temperature strength of the artificial dispersoid W alloys made thus far. As compared in the worked condition, its tensile strength at 2,500°F (1,370°C) is about 30% higher than that of unalloyed W, 67 k.s.i. vs. 49 k.s.i.

Regular alloy systems

Alloys such as W-0.6 Nb-0.004 C, W-0.9 Nb-0.018 C, and W-0.1 Zr-0.001 C results in improvements of 200-300% in tensile strength at 3,000°F (1,650°C) as compared with recrystallized W, 46-60 k.s.i. vs. 19 k.s.i. Further work is required to determine whether this is due to solid solution hardening, dispersion hardening or a combination of the two. No improvement over unalloyed W was found to result from the addition of 0.07% Ti even with 0.003% C present. Whether higher Ti and/or C would be more effective has not been determined.

The W-30 Re alloy possesses a tensile strength at 3,000°F (1,650°C) comparable with the W-0.9 Nb and W-0.1 Zr alloys. The high elevated temperature strength of the W-30 Re alloy is apparently due to solid solution hardening. Its room temperature elongation of 5% is unusually high compared with commercial grades of unalloyed W. The beneficial effect of Re on ductility is believed to be associated with a change in interfacial energy, which prevents formation of the continuous grain boundary oxide films usually present in unalloyed W.

The main barrier to the evaluation of other W-base alloys containing substantial amounts of substitutional elements has been difficulty in primary working. Thus far evaluation of such alloys has been restricted to hot hardness testing.

STATUS OF Mo ALLOYS

Properties of unalloyed Mo metal

As shown in Table II, the tensile strength of unalloyed Mo at 2,000°F (1,095°C) is 25 and 40 k.s.i. in the recrystallized and worked conditions, respectively. In the recrystallized condition, the rupture strength at this temperature is 12 k.s.i.

TABLE II
MECHANICAL PROPERTIES OF MO AND MO-BASE ALLOYS

Alloy	Condition*	Test temp. (°F)	Approx. Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El. (%)	R.A. (%)	100-hour R.S. (k.s.i.)
Mo	AC-R	1,800	18	35	41	98	15
"	"	2,000	16	25	71	97	12
"	AC-W	2,100	31	32	45		
Mo	AC-W	1,800		45	30		
"	"	2,000		40	40		
"	"	2,500		15	53		
"	"	2,750		11	53		
"	"	3,000		6.7	59		
0.1 ZrO ₂	PM	2,000					24
20 Re	AC-R	70		175	20		
"	"	2,000		40	23		20
"	"	2,400		20	25		
"	"	3,000		15	31		
0.5 Ti-0.02 C	AC-W	1,800		65	25		53
"	AC-W	2,000		60	15		34
"	"	2,200		50			
"	"	2,400		20	71		
"	"	2,500		21	71		
"	"	2,750		15	53		
"	"	3,000		9.8	56		
1.25 Ti-0.04 C	AC-R	1,600		46			40
"	"	1,800					38
"	"	2,000					20
3.2 Ti-0.50 C	AC-SR	74	127	135	23	20	
"	"	1,800	44	59	23	57	44
"	"	2,400	26	36	53	93	10
0.05 Zr-0.02 C	AC-SR	74	116	126	13		
"	"	1,800		80	2		56
"	"	2,400		21	14		
0.4 Zr-0.05 C	AC-SR	74	108	123	28	55	
"	"	1,800	63	77	19	39	61
"	"	2,400	35	57	25	84	14
1.4 Nb-0.05 C	AC-SR	74	108	128	4	3	
"	"	1,800	63	87	17	56	69
"	"	2,400	14	24	77	95	12
1.45 Nb-0.25 C	AC-SR	75	120	156	1	0.8	
"	"	1,800	86	101	7	14.5	80
"	"	2,400		64	36	88	12
0.46 Ti-0.07 Zr-0.02 C	AC-SR	76	100	130	29	63	
"	"	1,800		86	18	73	70
"	"	2,400		54	31	96	
"	"	3,000		14			
1.27 Ti-0.29 Zr-0.30 C	AC-SR	70	98	121	1	0.5	
"	"	1,800		91	11	44	
"	"	2,400	41	61	26	61	33
"	AC-R	70	55	87	5	4	
"	"	1,800		61	29		55
"	"	2,400		46	41		26
1.25 Ti-0.20 Zr-0.15 C	AC-W	75	112	136	22		
"	"	1,800	61	68	20		61
"	"	2,200	53	61	11		34

TABLE II (continued)

Ref.	Alloy	Condition*	Test temp. (°F)	Approx. Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El. (%)	R.A. (%)	100-hour R.S. (k.s.i.)
(10)	25 W-0.1 Zr-0.05 C	AC-R	75	79	105	32	25	
	"	"	1,800	23	43	46	91	34
	"	"	2,400	17	29	58	89	12
	25 W-0.1 Zr-0.05 C	AC-SR	75	137	141	0	0	
	"	"	1,800	90	98	18	67	73
	"	"	2,400		74	26	81	12
	25 W-0.5 Ti-0.05 C	AC-SR	74	125	146	17	35	
	"	"	1,800	51	93	13	27	68
	"	"	2,400		28	61	76	10

* PM, powder metallurgy; AC, as-cast; R, recrystallized; W, worked; SR, stress-relieved.

Artificial dispersoid systems

The addition of 0.1 ZrO₂ results in a rupture strength at 2,000°F (1,095°C) of 24 k.s.i., which is presumably higher than can be obtained with unalloyed Mo.

Regular alloy systems

As with the effect of Re on W, a Mo-20 Re alloy in the recrystallized condition possesses a substantially higher tensile and rupture strength at 2,000°F (1,095°C) 40 and 20 k.s.i., respectively, as compared with unalloyed Mo. This is believed to be due to the solid solution hardening effect of Re.

The most effective alloying elements in Mo from the standpoint of strengthening appear to be Ti, Nb and Zr. In the presence of relatively small amounts of carbon, Ti and Nb exert large strengthening effects that are mainly attributable to dispersion hardening associated with the presence of fine carbides. As indicated by the fact that only coarse carbide agglomerates have been observed, Zr appears to exert its influence mainly by solid solution hardening.

For a given Ti content, the strengthening effect increases with carbon content and reaches a maximum at a C/Ti ratio of about 0.15. This is 60% of the stoichiometric ratio corresponding to TiC. It seems likely that below a C/Ti ratio of 0.15, fine TiC particles may predominate; whereas above this ratio, coarser Mo₂C particles may predominate. A Mo-0.5 Ti-0.02 C alloy (C/Ti ratio = 0.04) in the worked condition exhibits improvements over unalloyed Mo of about 150% in tensile strength, 60 vs. 40 k.s.i., and 300% in rupture strength, 34 vs. 12 k.s.i., at 2,000°F (1,095°C). About 75% higher tensile strength at 2,400°F (1,315°C) can be obtained with a worked Mo-3.2 Ti-0.50 C alloy (C/Ti ratio = 0.16) 36 vs. 20 k.s.i.

A small amount of Zr (0.05%) appears to be extremely effective in increasing strength. At 1,800°F (980°C), a Mo-0.05 Zr-0.02 C alloy exhibits about 100% higher tensile strength (80 vs. 45 k.s.i.) than unalloyed Mo in the worked condition. Increasing both Zr and C (Mo-0.4 Zr-0.05 C) results in higher strength at 2,400°F (1,315°C) than does the Mo-0.05 Zr-0.02 C alloy as compared in the worked condition, 57 vs. 21 k.s.i.

A Mo-1.4 Nb-0.05 C alloy in the worked condition possesses a tensile strength at 1,800°F (980°C) of 63 k.s.i., which is comparable with that of the Mo-0.05 Zr-0.02 C alloy. A Mo-Nb alloy of higher carbon content (Mo-1.45 Nb-0.25 C) has a tensile and rupture strength in the worked condition of 101 and 80 k.s.i. respectively. These

the highest values reported for any of the Mo alloys. At 2,400°F (1,315°C), this alloy maintains a high tensile strength, 64 k.s.i., although the rupture strength drops to 12 k.s.i.

Combinations of Ti and Zr appear very effective. In the worked condition, a Mo-0.46 Ti-0.07 Zr alloy exhibits tensile strengths of 86 and 54 k.s.i. at 1,800°F (980°C) and 2,400°F (1,315°C) respectively. Increasing the Ti, Zr, and C contents to Mo-1.27 Ti-0.29 Zr-0.30 C results in the highest rupture strength at 2,400°F (1,315°C) reported for an Mo alloy, 52 k.s.i. in the worked condition. Even in the recrystallized condition, the tensile strength of the Mo-1.27 Ti-0.29 Zr-0.30 C alloy at 1,800°F (980°C) is about 150% greater than that of unalloyed Mo, 91 vs. 35 k.s.i. This alloy in the recrystallized condition is as strong at 2,400°F (1,315°C) as unalloyed Mo in the worked condition tested at 1,800°F (980°C). These comparisons illustrate that a combination of solid solution and dispersion hardening can result in a much greater strengthening effect than can be obtained by subjecting unalloyed Mo to strain hardening alone.

A Mo-25 W-0.1 Zr-0.05 C alloy has been found to possess the highest tensile strength at 2,400°F (1,315°C), 74 k.s.i., reported thus far for any Mo alloy in the worked condition. Apparently, solid solution hardening due to the combination of W and Zr is responsible. The contribution of working to strength is indicated by a comparison of the Mo-25 W-0.1 Zr-0.05 C in the worked and recrystallized conditions. At 2,400°F (1,315°C), the recrystallized alloy exhibits a tensile strength of only 29 k.s.i. The substitution of 0.5 Ti for 0.1 Zr results in a much lower tensile strength at 2,400°F (1,315°C). Thus a Mo-25 W-0.5 Ti-0.05 C alloy in the worked condition possesses a tensile strength of only 28 k.s.i. It appears that Zr is a more potent element than Ti, even though the latter presumably makes some contribution to dispersion hardening.

The lack of correlation between tensile strength and rupture strength should be noted. The Mo-25 W-0.1 Zr-0.05 C alloy in the worked condition exhibits a high tensile strength, 74 k.s.i., but a low rupture strength, 12 k.s.i. at 2,400°F (1,315°C). On the other hand, the Mo-1.27 Ti-0.29 Zr-0.30 C alloy in the worked condition exhibits a high rupture strength, 33 k.s.i., and a lower tensile strength, 61 k.s.i., at the same temperature. Apparently, the occurrence of dispersion hardening in the latter alloy makes a large contribution to rupture strength. This correlates with the fact that the Mo-1.27 Ti-0.29 Zr-0.30 C alloy has a higher recrystallization temperature than the Mo-25 W-0.1 Zr alloy.

STATUS OF Ta ALLOYS

Properties of unalloyed Ta metal

As shown in Table III, unalloyed Ta is relatively weak at elevated temperatures. For example, the tensile strength of high purity tantalum at 2,190°F (1,200°C) is only about 17 k.s.i. after cold working. With higher interstitial contents, particularly carbon, rupture strength improves. The rupture strength for Ta-0.006 C is 300% higher at 2,190°F (1,200°C) than high purity Ta, 9.6 vs. 3.2 k.s.i. There is some evidence that carbide precipitation is involved. The solubility of carbon in Ta at 2,190°F (1,200°C) is reported to be only about 0.009%, whereas the solubilities for N and O are much higher (0.44% and 0.26%, respectively).

TABLE III
MECHANICAL PROPERTIES OF Ta AND Ta-BASE ALLOYS

Ref.	Alloy	Condition*	Test temp. (°F)	Approx. Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El. %	100-hour R.S. (k.s.i.)
(6)	Ta**	PM-R	1,800	12	22	33	7***
	"	"	2,000	8	17	43	3***
	"	"	2,200	7.5	15	48	
	"	"	2,500				1***
(12)	Ta	EB-R	2,190		11	45	3.2
	"	EB-W	2,190		17	6	
	Ta-0.096 C	AC-W	2,190				9.6
	Ta-0.026 N	"	2,190				3.6
	Ta-0.0560	"	2,190				3.2
	10 Ti	AC-W	2,190		25	12	
	5 Hf	AC-R	75	34	45	27	
	"	"	2,190		40	30	
	"	AC-W	2,190		52	15	
	10 W	AC-R	75	70	80	16	
	"	"	2,190		42	13	
	30 Nb	AC-W	2,190		22	10	
	20 Nb-10 Ti	AC-W	2,190		18	14	
	30 Nb-5 Zr	AC-R	75	60	74		
	"	"	2,190		38	4	
	30 Nb-10 Cr	AC-R	2,190		24	37	
	30 Nb-10 Hf	AC-R	75	53	65		
	"	"	2,190		38	30	
	30 Nb-10 Mo	AC-R	2,190		32	4	
	30 Nb-10 W	AC-R	75	65	65	2	
	"	"	2,190		28	22	
	"	AC-W†	2,190		43	7	
	30 Nb-5 V	AC-R	75	78	96	22	
	"	"	2,190		41	53	
(26)	Ta-10 W	AC-W††	72	164	180	4	
	"	"	1,800	80	94	4.2	
	"	"	2,200	47	67	4	
	"	"	2,600	14	21	17	
	"	"	3,000	12	12	33	

* R, recrystallized; W, cold worked 50%; EB, electron beam melted; PM, powder metallurgy
AC, arc-cast.

** p.p.m. C, 130 p.p.m. N, 56 p.p.m. O.

*** SCHMIDT¹²

† Pack rolled at 1,800°F

†† Cold reduced 94%

Regular alloy systems

Most of the work reported on Ta-base alloys so far has been on regular alloy systems. The important binary systems that have been evaluated for elevated temperature mechanical properties are Ta-W, Ta-Ti, Ta-Hf, and Ta-Nb. A Ta-7.5 W alloy has been used commercially for a long time as a high temperature spring in vacuum tubes. In the recrystallized condition, a Ta-10 W alloy has a tensile strength at 2,190°F (1,200°C) of 42 k.s.i., whereas after cold working 94%, the tensile strength is increased to 67 k.s.i. Relatively high strength, 12 k.s.i., is maintained on heating the cold-worked Ta-10 W alloy up to 3,000°F (1,650°C). On the basis of

in temperature tensile tests, it appears that Mo has essentially the same solid solution hardening effect as W provided that alloy content is measured on an atomic basis.

As compared with unalloyed Ta in the worked condition, the improvement in tensile strength due to 5% Hf is approximately 300% at 2,190°F (1,200°C), 54 *vs.* 14 k.s.i. Considering the fact that the Ta-5 Hf alloy was cold worked 50% whereas the Ta-10 W alloy was cold worked 94%, Hf is a more potent alloying element than W. Several ternary alloys containing 20-30% of Nb and 5-10% of Ti, Zr, V, Cr, Mo and Hf have recently been evaluated at 2,190°F (1,200°C). The best ternary alloy

TABLE IV
MECHANICAL PROPERTIES OF Nb AND Nb-BASE ALLOYS

Designation	Alloy	Condition ^a	Temp. (°F)	Approx. Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El. (%)	K.A. (%)	100-hour R.S. (k.s.i.)
{	Nb	AC-W	1,800	8	14	55	99	
	"	"	2,000	6	10	50	80	
	"	"	2,200	4	9	45	70	
	Nb*	AC-R	2,000	8.1	10.1	34	100	
	"	"	2,200	7.5	9.3	21	73	
	"	"	2,400	4	5.5	70	82	
	"	"	2,500	2.8	3.9	97	100	
	10 Ti	?	1,800					13
	"	"	2,200		17	18		
	5 Mo	"	70	49	59	8		
	5 Mo	"	2,200	8	20			
	5 V	"	80	74	86			
	"	"	2,000	34	37			
	10 W	"	70	58	67	10		
	10 W	"	2,000	16	19			
	10 Zr**	"	70	61	83	7		
	"	"	2,000	38	48	28		
<i>Westinghouse Alloys</i>								
{	NC-9	5 Ti-5 Zr	?	75	54			
	"	"	"	2,000	26	22		
	NC-31	5 Mo-5 Hf	"	2,000	43			
	NC-32	5 Hf-1 Ti-1 Zr	"	75	77	26	42	
	"	"	"	2,000	47	49	25	
	"	1 Ti-1 Zr-1 Hf	"	2,000	43	44	99	
	NC-155	5 V-5 Mo	AC-R	75	77	95	29	37
	"	"	"	75	37	40	44	54
	NC-181	5 V-5 Mo-1 Zr	AC-R	2,000	51	54	5	6.2
	VAM 19	5 Hf-2 Mo	AC-SR	75	70	83	12	56
	"	"	"	2,000	39	41	14	50
<i>General Electric Alloys</i>								
{	F-44	15 Mo-1 Zr	?	2,000	65			30
	F-48	15 W-5 Mo-1 Zr	AC-W	75	86	125	25	
	"	"	"	2,000	42	65	19	35
	"	"	"	2,200	30	48	21	17
	"	"	"	2,400	15	31		
	F-50	15 W-5 Mo-5 Ti-1 Zr	AC-W	75	80	122	24	
	"	"	"	2,200	23	50	28	20
	"	"	"	2,200	27	35	35	11
	"	"	"	2,400	18	21	45	
	"	"	"	"	"	"	"	"

TABLE IV (continued)

Ref.	Designation	Alloy	Condition [†]	Temp. (°F)	Approx. Y.S. (k.s.i.)	U.T.S. (k.s.i.)	El. (%)	R.A. (%)	100- K (k.)
<i>C. Fansteel Alloys</i>									
(24)	F82	32.5 Ta-0.75 Zr	AC-W	75		80	3		
	"	"	"	2,000	40	45	8		
	F83	***	AC-SR	2,000		45			
	"	"	"	2,200	34	38	16		
	"	"	"	2,500	19	26	28		
(24)	D3I	10 Mo-10 Ti	AC-E	75	92	100	22		47
	"	"	"	1,800					
	"	"	"	2,000	33	35	12		9
	"	"	"	2,200	22	25	14		13
	"	"	"	2,200†	26	27	22		
	"	"	"	2,400		20	8		11
	"	"	"	2,575		11			40
	D4I	20 W-10 Ti-6 Mo	AC-E	75		125	10		
	"	"	"	2,000		50	25		
	"	"	"	2,000†	53	57	26		57
	"	"	"	2,300	32	36	30		
	"	"	"	2,500		25	35		
<i>E. Union Carbide Alloys</i>									
(24)	Cb-6	8 Ti-10 W	AC-W	1,830	22	33	44		
	"	"	"	2,200		17	52		
	Cb-7	7 Ti-28 W	AC-W	75	140	146	3.8		5.2
	"	"	"	1,830	41	56	49		78
	"	"	"	2,200	38	41	22		75
	Cb-16	20 W-10 Ti-3 V	AC-E	1,830	68	77	15		54
	"	"	"	2,200	27	34	40		82
	Cb-20	5 Ti-5 Zr-15 W	AC-E	75	128	131	3.3		5.4
	"	"	"	1,830	69	76	20		48
	"	"	"	2,200	26	32	17		52
	Cb-22	3 Al-3 V	?	75	126	133	7		6.2
	"	"	"	1,830	32	33	88		82
	"	"	"	2,200	13	13	78		92
	Cb-24	7 Ti-3 Al-3 V	AC-W	75	148	155	5		9.8
	"	"	"	1,830	25	26	78		93
	"	"	"	2,200	8	8.4	1.2		100
	Cb-56	3 Al-3 V-1 Zr	AC-W	1,830	32	37	52		
	Cb-67	7 Ti-3 Al-3 V-1 Zr	AC-W	1,830	25	29	52		56
	"	"	"	2,200	6	7	68		63
	Cb-74	5 Zr-10 W	AC-E	2,200	42	45	23		
	Cb-65	7 Ti-0.8 Zr	AC-W	75	86	96	20		66
	"	"	"	1,800	21	28	14		96
	"	"	"	2,000	11	16	71		99
	"	"	"	2,200	6.5	9.5	88		99
	"	"	AC-R	75	56	72	35		80
	"	"	"	1,800	22	36	31		72
	"	"	"	2,000		23	25		92
	"	"	"	2,200		15	42		96

† AC, arc-cast; R, recrystallized; W, worked; SR, stress-relieved; E, extruded.

* C, 240 p.p.m.; N, 190 p.p.m.; O, 240 p.p.m.

*** Modified F82 containing Ti.

** Westinghouse Alloy NC-21

† In vacuum

appears to be Ta-30 Nb-5V, which in the recrystallized condition exhibits a tensile strength of 41 k.s.i.

In summary, it appears that the most effective mechanism of strengthening Ta by alloying is solid solution hardening involving relatively large amounts of such alloying elements as W, Hf, Nb and V. Although the mechanism of dispersion hardening is potentially operative in Ta-base alloys, it is just beginning to receive attention. There are indications that small amounts of Ti and Zr in combination with C result in significant dispersion hardening effects.

STATUS OF Nb ALLOYS

Properties of Nb metal

As shown in Table IV, Nb in the worked condition varies from a tensile strength of 14 to 9 k.s.i. over the range 1,800-2,200°F (980-1,205°C). As with Ta, the room temperature ductility of Nb is relatively high and much less sensitive to the presence of C as compared with W and Mo.

Regular alloy systems

The main binary systems that have been evaluated for high temperature strength are Nb-W, Nb-Mo, Nb-Ti, Nb-V, Nb-Zr and Nb-Hf. As shown in Fig. 1, the most effective strengtheners at 2,000°F (1,095°C) are V and Zr. The limiting factor in the use of these elements appears to be low ductility at elevated temperatures of about 15% V and 5% Zr. The alloying elements W, Mo and Hf appear to be roughly equivalent with respect to strength at 2,000°F (1,095°C) and no adverse effect on ductility is indicated in Fig. 1. The use of Mo above about 5% has been found to result in a marked lowering of oxidation resistance. Additions of Ti up to about 1% are just as effective as W or Mo. Beyond this amount, the rate of strengthening decreases, presumably owing to the lowering effect that Ti has on the melting point of Nb. Al and Cr are known to be beneficial from the standpoint of oxidation resistance. The limitation in the use of Al is presumably lowering of the melting point, whereas Nb has the disadvantage that brittle intermediate phase occur in the Nb-C system. Considerable effort has gone into the development of Nb alloys containing two or more alloying elements. The interstitial contents of these alloys are generally in the following ranges: 0.02-0.08% carbon, 0.01-0.02% nitrogen and 0.02-0.08% oxygen. In these interstitial ranges, C is most likely to exceed its solid solubility. The solubility of C in Nb at 2,190°F (1,200°C) is about 0.014% as compared with 0.24 and 0.52% for N and O respectively.

The size, distribution, and composition of the carbide phase in a Nb alloy depends on the over-all composition. For F48 (Nb-15 W-5 Mo-1 Zr), the carbides contain W and are finer and greater in number than those in F50 (Nb-15 W-5 Mo-5 Ti-1 Zr) which contain both Zr and Ti. This may account for the higher strength at 2,200°F (1,205°C) of F48 as compared with F50 in the worked condition, 48 vs. 35 k.s.i.

Dispersion hardening associated with formation of carbides is believed to also occur in such alloys as Cb-16, Cb-65 and D 41. In the extruded condition, Cb-16 (Nb-20 W-3 Ti-3 V) has a higher tensile strength at 1,830°F (1,000°C) than in the worked condition, 77 vs. 56 k.s.i. Evidently, solution of carbon occurs on heating to the extrusion temperature of 2,900°F (1,595°C), and the higher carbon matrix is retained on the relatively fast cool to room temperature. The increased strength is developed

on subsequent heating to the test temperature, which apparently allows carbide precipitation to occur. Similarly, alloy Cb-65 (Nb-7 Ti-0.8 Zr) initially in the worked condition exhibits a higher tensile strength at 2,000°F (1,095°C) following a recrystallization temperature of 2,600°F (1,425°C) as compared with 2,200°F (1,205°C), 23 vs. 16 k.s.i. The D-31 alloy (Nb-10 Mo-10 Ti) has been reported to increase in strength after a similar "heat treatment".

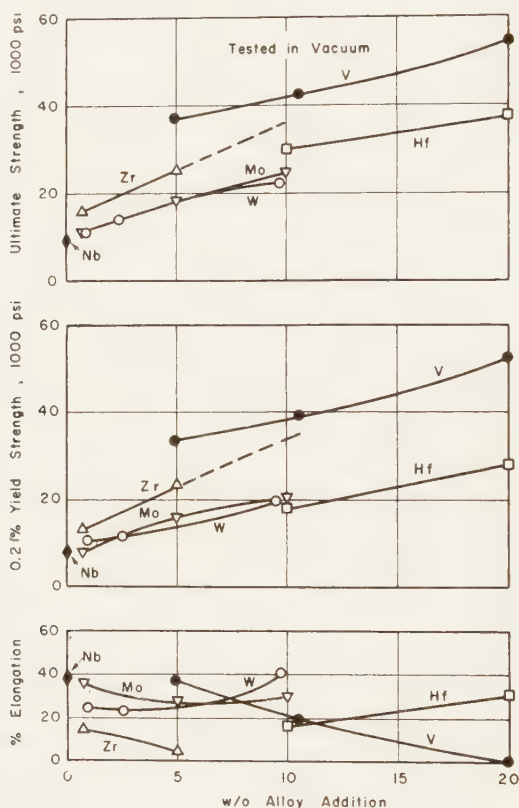


Fig. 1. Tensile properties of niobium binary alloys of 2,000°F (ref. 25, crystallized condition).

The use of Ti improves oxidation resistance and workability, but is disadvantageous with respect to high temperature strength. In order to compensate for this, the trend has been to use relatively large amounts of W in conjunction with Ti alloys such as Cb-16 (Nb-20 W-10 Ti-3 V), Cb-7 (Nb-28 W-7 Ti) and D-41 (Nb-20 W-6 Mo-10 Ti) are examples. As compared with unalloyed Nb, substantial improvements in oxidation resistance have been obtained with such alloys.

CONCLUSIONS

Improvements attainable by alloying

The known ultimate tensile strength values for the three "best" W, Mo, Ta and Nb-base alloys at selected temperatures are plotted in Fig. 2. It should be noted that



Fig. 2. Reported tensile strength of "best" W, Mo, Ta and Nb-base alloys. ○, W-base alloys; ◐, Mo-base alloys; ●, Ta-base alloys; ⊗, Nb-base alloys.

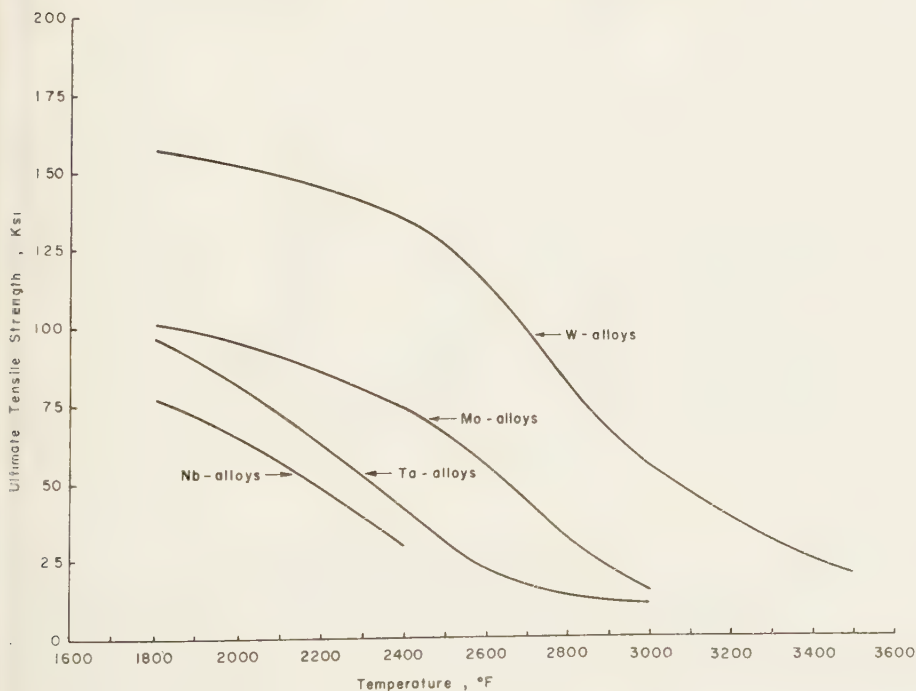


Fig. 3. Estimated tensile strengths attainable with "best" W, Mo, Ta and Nb-base alloys.

data pertaining to a given alloy are not available over the complete range of 1,800°F (980°C) to 3,500°F (1,930°C) covered in Fig. 2. This means that the alloy of a given base metal that is plotted as "best" at a particular temperature may actually be inferior to a known alloy of the same base metal which was not tested at the temperature in question. For example, the W-0.57 Nb alloy which was only tested at 3,000°F (1,650°C) is probably superior to the W-0.4 TaC alloy at 2,500°F (1,370°C). Since there

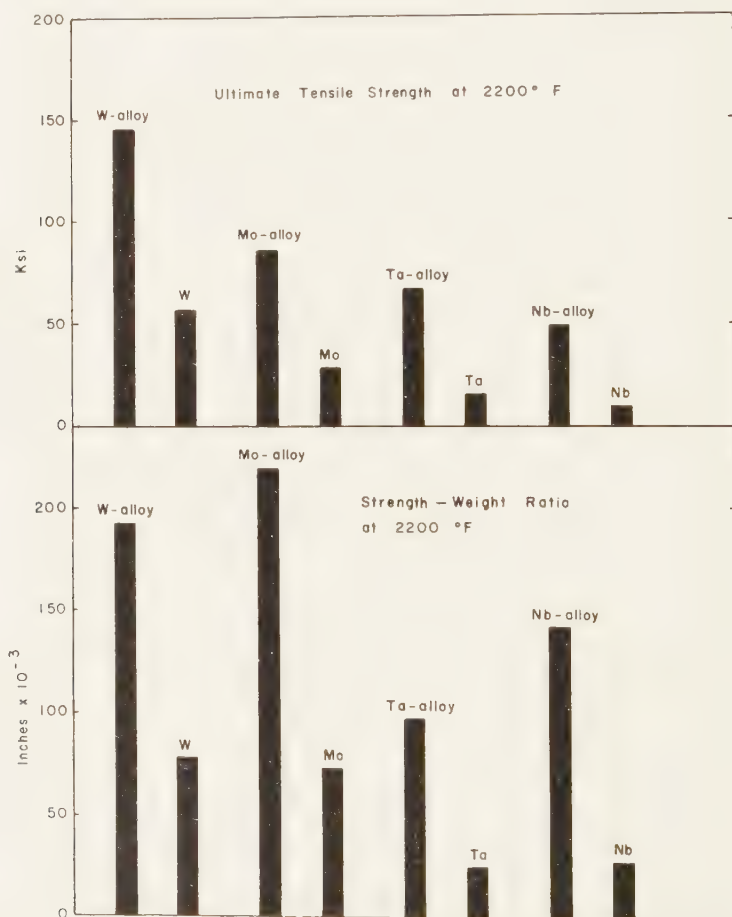


Fig. 4. Comparisons of tensile strengths and strength-weight ratios of W, Mo, Ta and Nb with their "best" alloys at 2,200°F.

are no data to substantiate this, the W-0.4 TaC is plotted as best at 2,500°F (1,370°C).

In contrast with Fig. 2, Fig. 3 gives estimated attainable tensile strengths over as wide a temperature range as is considered suitable for each group of alloys corresponding to a given base metal. On this basis, the order of superiority is as follows: W-base, Mo-base, Ta-base and Nb-base alloys. Considering the fact that such variables as extent of plastic deformation, carbon content, optimum alloy levels, method of fab-

ation, and tensile testing procedure still should be investigated in greater detail, it is likely that even higher tensile strengths can be attained. Under optimum conditions, the curves in Fig. 3 can probably be raised by at least 20%.

Comparisons of the "best" W-base, Mo-base, Ta-base, and Nb-base alloys at 2,200°F (1205°C) are facilitated by Fig. 4. The upper chart is based on tensile strengths and general comparisons can be made. The improvements derived by alloying (comparison of "best" alloy with unalloyed base metal) are as follows: alloying of W, 150%; of Mo, 200%; of Ta, 300%; and of Nb, 500%. Compared with the "best" Nb-base alloy, the superiority of each other "best" alloy is as follows: "best" W alloy, 200%; "best" Mo alloy, 75%; and "best" Ta alloy, 15%.

The lower chart of Fig. 4 is based on strength-weight ratios. The improvements in strength-weight ratios derived by alloying are essentially the same as the corresponding improvements in tensile strength because the change in density by alloying is not significant. On the other hand, the strength-weight ratios of the "best" alloys put them in a different order than on the basis of tensile strength. The lowest strength-weight ratio is exhibited by the "best" Ta-base alloy. Compared with the "best" Nb-base alloy, the superiority of other "best" alloys is as follows: Mo-base, 120%; W-base, 100%; and Nb-base, 45%.

Metallurgical effects

The most important metallurgical effects associated with the high temperature strengthening of refractory metals by alloying are considered to be as follows:

(a) Three mechanisms of strengthening are operative: dispersion hardening, solid solution hardening and strain hardening. The observed strength is usually a combination of 2 or 3 of these mechanisms.

(b) The relative contribution of each mechanism depends on the particular base metal, type and amount of alloying and interstitial elements, and extent of working.

(c) With respect to effectiveness of dispersion hardening at high temperatures, carbon appears to be more important than other interstitial elements.

(d) For the group VIA metals (W and Mo), relatively small amounts of alloying elements of larger atomic size (Zr, Nb and Ti) are found to confer considerable strengthening. These elements either result in greater strain hardening due to plastic deformation or contribute to dispersion hardening associated with the occurrence of the carbides.

(e) For the group VA metals (Ta and Nb), relatively large amounts of alloying elements are required to confer considerable strengthening. Hf has been found most potent for Ta and V for Nb. The main mechanism appears to be solid solution hardening. In some Ta and Nb alloys, dispersion hardening associated with carbide precipitation can make a large contribution.

Future work

In order to develop even stronger refractory alloys, the mechanical properties of more alloy systems should be determined. Research and development programmes should be aimed at determining the role of dispersion, solid solution, and strain hardening in these systems. Studies of the specific contributions of alloying and interstitial elements to these hardening mechanisms should be included. In addition, greater

attention should be given to such phenomena as substructure formation during recovery and the occurrence of fibreing by plastic deformation.

Further attention should be paid to known systems in order to obtain further improvements in mechanical properties. The optimum amounts of carbon and alloy elements should be determined more closely. The problem of reproducibility of mechanical properties requires attention. For example, it is known that surface condition is an important variable and contamination should be avoided. A build-up of interstitials at the surface can result in embrittlement, raise the recrystallization temperature, and retard grain growth. Furthermore, the effects of processing variables have to be determined in order to ensure that the desired level of mechanical properties are consistently attained.

In investigating known or unknown alloy systems, it is important to obtain the following types of information:

- (a) effect of purity, melting, primary working and fabrication procedures;
- (b) effect of section size and direction;
- (c) effect of working and annealing treatments;
- (d) transition temperatures as a function of strain rate, notch severity and method of testing;
- (e) complete room temperature tensile properties including uniform elongation and strain-hardening characteristics;
- (f) complete elevated temperature mechanical properties including rupture strength and creep rate over wide ranges of temperatures and times.

To accumulate all the information desired represents a tremendous amount of work. However, there appears to be no alternative for obtaining a sound basis for scientific and engineering judgments relative to the "big-four" refractory alloys.

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COMPRESSION CREEP TESTS ON NIOBIUM AT HIGH TEMPERATURES

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SUMMARY

Details are given of a machine for measuring creep in compression at high temperatures in a vacuum of about 10^{-6} mm of Hg. The design is such that the maximum temperature of testing is limited mainly by the creep strength of the push rods; rods of recrystallized alumina are satisfactory at $1,200^{\circ}\text{C}$. Creep curves are given for a commercial grade of niobium.

INTRODUCTION

It is possible that niobium alloys will prove satisfactory materials for use at high temperatures, and details of their creep behaviour are required. In this paper a compression creep testing machine suitable for this work is described, and some results for niobium of commercial purity are given. A compression machine was chosen for reasons which have been given by SULLY¹. In particular, small specimens with a simple shape can be used, and the difficulties associated with the use of grips at high temperatures are avoided.

An acceptable alloy will require a satisfactory resistance to oxidation, but it is useful to separate the two aspects of the problem in the first instance, and all tests have been made in a good vacuum.

EXPERIMENTAL

The creep machine

The machine is shown diagrammatically in Figs. 1a and 1b. The specimen is compressed between rods of recrystallized alumina (Fig. 1a). The lower rod is supported by a framework which is made from a heat-resistant alloy*. The upper rod passes through a water-cooled bellows, and is fixed to a steel rod with a collet. The steel rod is supported by two guides (Fig. 1b). In each guide the rod is nipped between the outer faces of three equally spaced ball bearings which rotate about axes at right angles to the axis of the rod. Each bearing has a screw adjustment so that the rod can be centred. No play is present in the guides, and friction is negligible in comparison with the loads used.

The load is applied through a lever which pivots on knife-edges and has a ratio of

* The alloy "G32" made by Jessop-Saville Ltd., Sheffield.

1. The springs are adjusted to balance the weight of the beam, and the load on specimen due to atmospheric pressure.

The strain is obtained from the movement of the lever, which is read on a dial gauge, and also automatically recorded. As the beam falls, it deflects a phosphor-bronze strip to which four strain gauges are attached in a bridge arrangement. The bridge is unbalanced by the deflection of the strip, and the resultant potential is registered on a millivolt recorder. The values of the applied loads, and of the strains obtained from the dial gauge readings, were checked by measuring the elastic deflection of a small calibrated beam, which was substituted for a specimen.

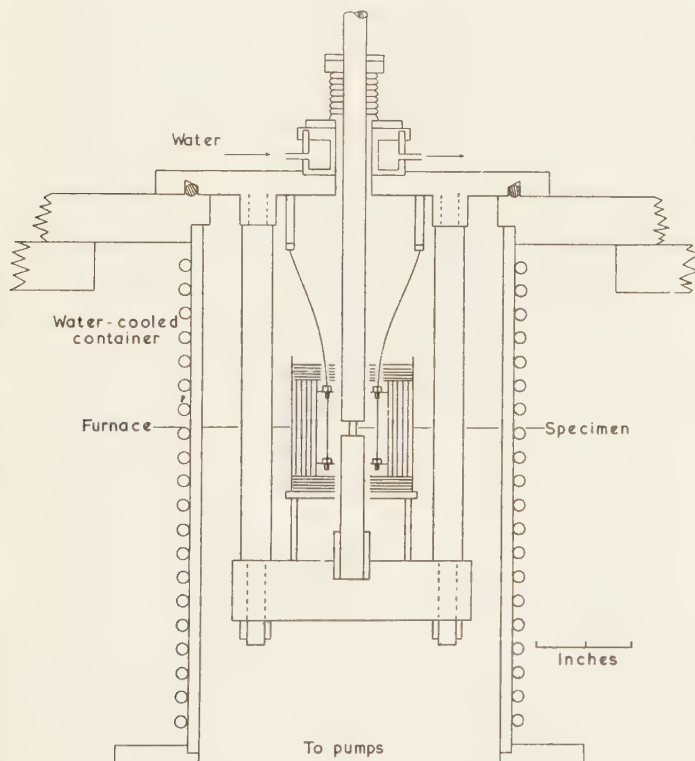


Fig. 1a. Diagram of the creep testing machine.

The furnace rests on a stainless steel stand, and is thermally insulated from it with alumina beads. The frame is made from tantalum sheet 0.010 in. thick, and is formed from two circular end plates spot-welded to tantalum struts. The vertical winding is tantalum wire 0.020 in. diameter, and is insulated from the frame by alumina beads. Five radiation shields are used, of which the inner two are tantalum, and the remainder nickel. The power input is regulated by a temperature controller of the proportional type* with a "Variac" in the output circuit. At 1,200°C the input is about 100 watt at 16 volt. The furnace has a very low thermal capacity, but with the control described, the variation in temperature is within 3°C. The temperature of the specimen is measured with two platinum/platinum-13% rhodium thermocouples

pressed against its surface. The thermocouples enter the furnace through twin-bore alumina tubes which are wired to the lower rod with tantalum wire. Preliminary tests with thermocouples spot-welded to a specimen showed that the temperature variation along its length was about 1°C .

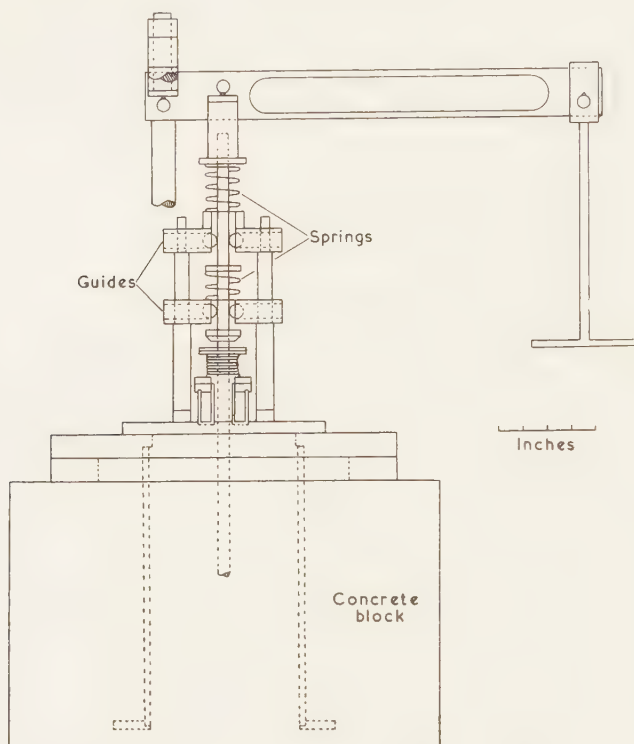


Fig. 1b. Diagram of the creep testing machine.

The temperature of the supporting framework becomes constant after several hours, but on loading a further increase of up to 10°C occurs during a period of about two hours. This effect is probably due to improved thermal contact between the lower alumina rod, and the framework. The rise in temperature causes an apparent creep strain of up to 0.2%, but a correction can be made by measuring the length of the specimen at the end of the test. Recovery of any creep strain is prevented by cooling the specimen under load.

With the furnace at $1,200^{\circ}\text{C}$, the framework does not exceed 200°C , so that the maximum testing temperature is mainly limited by the creep strength of the alumina rods. Blank tests at $1,200^{\circ}\text{C}$ gave no measurable creep after 100 hours at a stress equivalent to 10,000 p.s.i. on the specimen.

The steel container is coated with a hot-setting silicone varnish to reduce outgassing, and it is continuously pumped by a fractionating oil diffusion pump with a rated speed of 170–200 litres per second at the baffle-valve inlet. The furnace can be heated to $1,200^{\circ}\text{C}$ in about $1\frac{1}{2}$ hours without exceeding a pressure of $5 \cdot 10^{-6}$ mm of Hg, and there-

* A "Gardsman Stepless Controller" made by The West Instrument Corporation.



2. Microstructure of niobium-unetched, (a) $\times 250$, (b) $\times 1,000$. Prepared by polish attack with 90 ml satd. soln. of FeCl_3 in water, 10 ml conc. HF , and 2 g "gamma" polishing alumina.

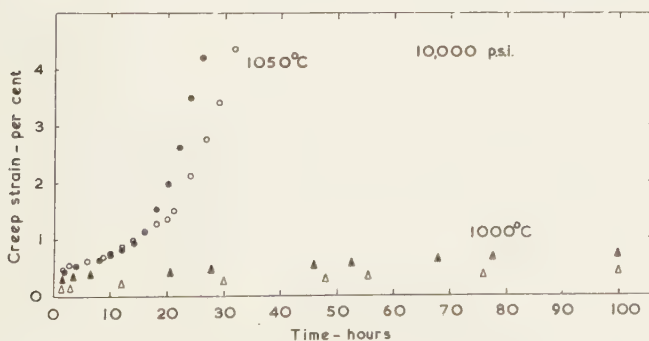


Fig. 3. Creep curves for niobium at a load of 10,000 p.s.i. Filled and open symbols represent duplicate tests.

after the pressure rapidly falls to less than 10^{-6} mm of Hg. At room temperature, with the baffle-valve closed, the rate of pressure increase in the container corresponds to a leak rate of about 0.01 micron litres per second.

To change specimens, the lever is removed, the furnace assembly is lifted from the container, and the furnace is raised to admit the specimen.

Specimens

Cylindrical specimens 0.18 in. diameter $\times$ 0.3 in. were slit from swaged rod prepared from an argon-arc melted ingot. They were surface ground to size, wrapped in niobium foil, and annealed in a vacuum of $5 \cdot 10^{-5}$ mm Hg for 2 h at $1,300^{\circ}\text{C}$.

Details of the specimens are given in Table I.

TABLE I

	Before testing	After testing
Ta %	0.2-0.25	—
C %	0.007-0.015	—
O ₂ %	0.076	0.078
Average grain diameter	0.067 mm	—
Average hardness D.P.N.	144	144

The hardness numbers and oxygen contents show that no significant contamination of the specimens occurred during testing.

The niobium contained a small quantity of an unidentified phase, which appeared in variable amounts in the specimens. A typical microstructure is shown in Figs. 2a and 2b.

Performance of the machine

Creep curves are shown in Fig. 3 for a constant load of 10,000 p.s.i. at $1,000^{\circ}$ and $1,050^{\circ}\text{C}$.

At $1,000^{\circ}\text{C}$ the creep strength is somewhat greater than that reported by ALLEN AND CARRINGTON for niobium of a similar nominal composition². This difference may be due to the unidentified phase in the present niobium.

At $1,050^{\circ}\text{C}$ a marked increase in the creep rate occurs after several hours. This effect may also be associated with the second phase, but further work is necessary to determine whether similar behaviour occurs in the absence of second phase, and tests are in progress on zone-refined niobium prepared by electron bombardment.

ACKNOWLEDGEMENTS

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THE INFLUENCE OF SMALL ADDITIONS OF NONMETALS AND METALS ON THE SINTERING, WORKING AND THE MECHANICAL PROPERTIES OF TUNGSTEN

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SUMMARY

The influence of 0.01–1.0 weight % of various elements on the sintering behaviour, the workability and the mechanical properties of tungsten has been examined. Carbon, boron, tungsten boride W_2B , tungsten silicide " W_3Si_2 ", aluminium, beryllium, titanium, zirconium, hafnium, thorium, vanadium and chromium were used as additives. Changes in the as-sintered density and hardness, workability by hot-rolling, hardness, transverse rupture strength and ductility (deflection on transverse bending) of worked alloys were determined and related to the concentration of alloying elements.

The effects of the added elements are considered in relation to the formation of volatile or solid refractory deoxidation products. Further work necessary to substantiate the limited data is suggested.

INTRODUCTION

The addition of small amounts of metal salts and oxides to tungstic acid prior to its reduction in hydrogen has long been industrial practice in the production of lamp filaments and electrode material. The additives used in the "doping" of tungsten serve (1) to restrain recrystallization, or (2) help to attain certain properties in recrystallized tungsten. Such measures are necessary because the intracrystalline strength of tungsten greatly exceeds the grain boundary (intercrystalline) strength, which is weakened by precipitation of minute quantities of oxide at the grain boundaries. This property of tungsten can be overcome either by creating a larger grain boundary area, by diluting the oxide film, or by aligning the grain boundaries parallel to the axis of the wire, and producing a stable (non-sag) structure.

Both means of improving the ductility of recrystallized tungsten are applied to tungsten containing oxide films. However, it is clearly preferable to eliminate these oxide films altogether so that these additives are not needed. Possible methods of elimination are (i) optimum purification of tungsten raw materials or (ii) deoxidation of tungsten during its production. Purification through deoxidation, i.e. by alloying with elements having a high affinity to oxygen, leads to either the elimination or the stabilization of impurities, mainly oxygen. It is surprising to see that the deoxidation of tungsten has so far not been a generally acknowledged practice, not even in a laboratory or pilot plant way. This may be because deoxidation as a solid state reaction

has so far not attracted the interest devoted to deoxidation reactions in the molten state. Most of the early work done to improve the workability of tungsten, for example the precipitation of sulphur, selenium, tellurium on the surface of tungsten during working², the addition of alumina or manganese oxide as decarburizers³ or the use of various etchants at intermediate stages of drawing⁴ neglects deoxidation as a procedure to purify tungsten.

To our knowledge, SMITHELLS⁵ first drew attention to the problem of deoxidizing tungsten by suggesting the addition of boron in order to facilitate the volatilization of impurities. (The use of boron as a deoxidizer has again been emphasized by LI AND WANG⁶.)

The beneficial effect of carbon (or a carburizing atmosphere during working) on the ductility and workability of tungsten has been patented⁷; the claim describes the swaging of tungsten after heating it in carbon-tube furnaces, *i.e.* in a carburizing deoxidizing atmosphere, thereby improving the ductility of tungsten rod and wire. SKAUPY⁸ has also mentioned the effect of carbon on the purification and improvement of the ductility of tungsten.

The addition of rare earth metals, and of boron carbide and tungsten-boride to deoxidize tungsten is under investigation in the United States¹.

In view of these scattered observations on the deoxidation of tungsten, it was decided to investigate systematically the deoxidizing influence of a number of metal and nonmetals. These were selected in view of their possible reactions with oxygen entrapped at tungsten grain boundaries, leading either to volatilization or to stabilization in the form of fine dispersions. Carbon, boron, silicon and aluminium were selected from the first point of view and beryllium, titanium, zirconium, hafnium and thorium from the second. Vanadium and chromium were also examined since both elements are completely soluble in tungsten and form less stable oxides.

EXPERIMENTAL TECHNIQUE

Raw materials used

The tungsten used in this investigation was produced from tungsten trioxide by reduction in hydrogen. The grain size, bulk volume, tap volume and chemical composition of the tungsten powder and the alloying element powders used are given in Table I.

Preparation of alloys

The powder additions were carefully mixed with tungsten powder in an agate mortar and the blends subsequently milled in carbide-lined ball mills for 30 minutes. A camphor-ether solution was added to the mixtures after milling to improve their pressability. Compacts 290 mm long and having a cross section of 8×8 mm were pressed with a total load of 120 tons, corresponding to a specific pressure of about 5 t/cm². The weight of the bars was 250 g. Table II gives the compositions of the specimens. Boron and silicon were also added in the form of tungsten boride and tungsten silicide powders which had been sintered, crushed and milled to achieve optimum distribution of boron and silicon. The bars were presintered at 1,200°C in a vacuum of approximately 10^{-5} mm Hg to permit safe handling. Direct sintering was carried out in hydrogen with a water-vapour content equivalent to approximately

GRAIN SIZE, BULK AND TAP VOLUME AND CHEMICAL COMPOSITION OF TUNGSTEN AND ALUAINING POWDERS

Element	Grain size (μ)	Bulk volume $\text{cm}^3/100 \text{ g}$	Tap volume	Chemical composition in %										
				C	O ₂	N ₂	Fe	Al	Si	Mg	Mn	Mo	Ni	Ca
W	3.48	58	28	<0.0005	0.19 0.20		0.0008				0.014			
C (lampblack)						0.01	—0.02	% slag		(Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃)	0.017			
B	1.12	560	300	0.09 0.08			0.50 0.50	0.03 0.03	1.54 1.58	6.6				
Si	20.88	110	70	0.02 0.02			<0.003	0.43 0.34						
Al	25.2	90	65				0.59 0.61		0.18 0.18	0.01		0.014	0.001	0.06 0.07
Be	10.8	180	96				0.22 0.25		0.06 0.08					5.50 5.24
Ti (hydride)	5.50	70	40	<0.005		0.056 0.056	0.23 0.22		0.04 0.04	<0.0001 0.024 <0.002 0.077 0.022				
Zr (hydride)	3.74	66	37	0.05 0.05			0.14 0.15							0.06
Hf (hydride)	—100 + 325 mesh	n.d.	n.d.	0.005	0.27	0.011	0.047	0.0025	0.005	0.001	0.001	0.001	<0.004	2.2% Zr
Th	6.5	36	24	0.11 0.13			0.046 0.048		0.24 0.28					0.01 0.02
V (hydride)	5.15	60	36	0.05 0.06			0.43 0.38		0.06 0.06					
Cr	11.29	36	22	0.002			0.007 0.011	0.01	0.01				0.04	0.02

* Residue after chlorination

TABLE II
CONCENTRATION OF ALLOYING ELEMENTS IN TUNGSTEN

Element	Weight %	
	Amounts added	After sintering
C	0.01	0.005/0.004
	0.1	0.023/0.020
B	0.01	
	0.1	n.d.
W ₂ B*	0.01	
	0.1	n.d.
	1.0	
"W ₃ Si ₂ "**	0.01	
	0.1	n.d.
	1.0	
Al	0.01	0.001
	0.1	0.001
Be	0.01	< 0.001
	0.1	< 0.001
Ti	0.01	0.011/0.010
	0.1	0.065/0.065
	1.0	0.64/0.64
Zr	0.01	traces
	0.1	0.006
	1.0	0.69/0.72
Hf	0.01	n.d.
	0.1	0.015
	1.0	0.26/0.27
Th	0.01	n.d.
	0.1	0.01
	1.0	0.64/0.63/0.66
V	0.01	0.01/0.01
	0.1	0.09/0.10
	1.0	0.83/0.87
Cr	0.01	0.0025/0.0032
	0.1	0.064/0.068
	1.0	0.54/0.56

*, ** Stoichiometric ratio in which B and Si were added.

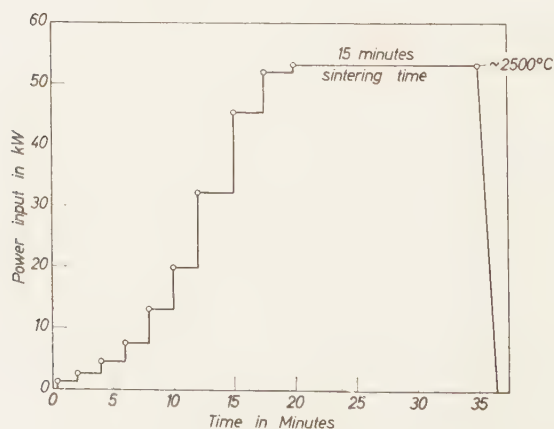


Fig. 1. Sintering schedule for the sintering of tungsten bars.

mg/m³ hydrogen. The sintering furnace was a two-bar type direct sintering bell with a maximum power input of 60 kVA at 32 volts. Two bars at a time were sintered according to the schedule shown in Fig. 1. Some deviations from this schedule occurred owing to the change in resistivity with increasing contents of the alloying elements. The bars were held for 15 min at the maximum measured temperature of approximately 2,500°C and the power then reduced to zero in about 1 minute. Bars were cooled to room temperature in 15 min.

Methods of analysis

Losses of alloying elements during sintering were examined and the final content of the various alloys analysed (see Table II). Boron and silicon contents could not be determined. Carbon was determined in a Ströhlein apparatus using the potentiometric method after oxidation of the sample at 1,400° in pure oxygen. Aluminium was determined gravimetrically in the residue after chlorination of tungsten at 450°C. Yttrium was analysed photometrically with Chromazurol S without separation from tungsten⁹. Titanium was analysed as Ti-EGTA-H₂O₂ chelate, vanadium as HEGTA-H₂O₂ chelate according to MARTINEZ AND CASTRO¹⁰. Chromium was determined photometrically with diphenylcarbazide without separation from tungsten. The method of analysis for zirconium, hafnium and thorium was developed in our laboratory¹¹ using the EDTA-titration of zirconium, hafnium and thorium after separation from tungsten by NH₃-precipitation.

Hot rolling of alloyed tungsten

The tungsten bars, which had an approximate cross section of 7 × 7 mm after sintering were hot-rolled from 1,600°C in a four-high rolling mill. They were given a reduction of 43% in one pass, yielding flat bars of a 4 × 10 mm cross section.

Testing procedure

The densities of the sintered bars were determined from the differences of their weight in air and water, and their hardnesses were measured as Vickers hardness using a 10 kg load.

Specimens for the examination of the mechanical properties of the worked flat bars were cut from the bars and fine-ground to exact dimensions, 2 × 2 × 22 mm. Hardnesses (VHN, 10 kg load), transverse rupture strengths and deflections on bending were measured, the latter on a Chevenard microtensile testing machine. The mechanical properties were determined in the as-rolled condition and after annealing the micro-test specimens at 1,000 and 1,500°C for 30 min. Measurement of tensile properties could not be carried out because of the considerable difficulties in preparing micro-tensile specimens with threaded shoulders.

RESULTS

Sintering behaviour

The sintering of the specimens was carried out without difficulty. Only with higher contents of Be, Ti, Zr, V and Cr could an evaporation of the alloying elements be observed visually. Changes in the resistivity of tungsten due to alloying elements resulted in a decrease of the maximum current needed to sinter at the average tempera-

ture of 2,500°C. The greatest effect was noted with 1% thorium, which caused a decrease of 21% in the usual maximum current of 2,100 A at approximately 27 V.

The external appearance of the sintered bars was good and comparable with pure tungsten except for an alloy with 0.1% aluminium which showed severe transverse cracking.

The properties of the sintered specimens are summarized in Table III. It appears that boron and silicon, when added in form of the boride or silicide, result in purer metal as judged by the fact that no chlorination residue could be found in these specimens. (The average chlorination residue of pure tungsten is 0.01–0.02%.) The addition of 0.1% of carbon and boron increases the hardness of the as-sintered tungsten by the formation of either carbide or a W-W₂B eutectic precipitated at the grain boundaries. Fig. 2 is a micrograph of the 0.1% carbon alloy showing the carbide particles along a grain boundary. Fig. 3 shows the W-W₂B eutectic in tungsten with 0.1% boron added. Aluminium does not show any significant effect on the as-sintered

TABLE III

DENSITY AND HARDNESS OF AS-SINTERED TUNGSTEN CONTAINING FROM 0.01–1.0 WEIGHT % OF VARIOUS ELEMENTS

<i>Alloying element</i>	<i>Weight %</i>	<i>Density (g/cm³)</i>	<i>VHN (10 kg load) (kg/mm²)</i>			<i>Average VHN (kg/mm²)</i>
Tungsten		18.2	288	288	288	288
C	0.004	18.47	286	308	322	305
	0.021	18.42	315	336	308	320
B	(0.01)*	18.53	297	308	297	302
	(0.1)	18.43	322	322	322	322
W ₂ B	(0.01)	18.57	286	286	274	282
	(0.1)	18.62	322	308	322	317
	(1.0)	18.38	274	286	308	290
"W ₃ Si ₂ "	(0.01)	18.67	322	303	297	307
	(0.1)	18.62	297	274	297	290
	(1.0)	18.57	254	274	297	275
Al	0.001	18.12	274	286	274	278
	0.001	17.75	(322)	193	(254)	—
Be	<0.01	18.41	297	297	297	297
	<0.01	18.21	297	274	274	282
Ti	0.01	18.76	322	308	308	318
	0.065	18.52	322	322	322	322
	0.64	17.74	274	274	274	274
Zr	traces	18.68	297	322	322	305
	0.006	18.45	308	322	308	318
	0.70	17.32	265	265	274	272
Hf	(0.01)	18.58	308	297	308	304
	0.015	18.46	274	274	274	274
	0.26	18.66	322	322	322	322
Th	(0.01)	18.38	308	286	297	298
	0.01	18.61	297	308	308	302
	0.65	18.38	308	308	297	302
V	0.01	18.60	322	308	322	317
	0.095	18.50	336	322	315	324
	0.85	17.80	286	297	308	298
Cr	0.0028	18.52	297	297	297	297
	0.066	18.44	274	286	274	284
	0.55	18.14	254	265	265	261

* not analysed. The values in () refer to amounts added.

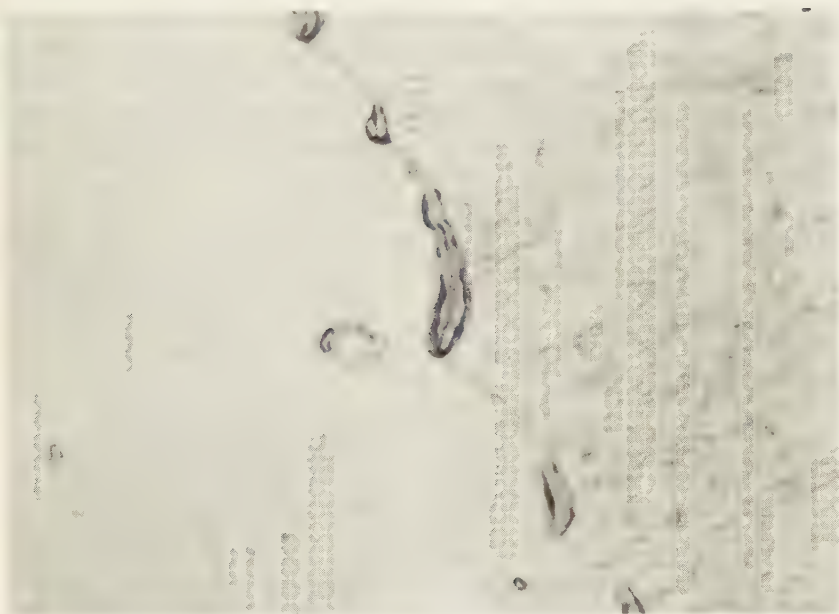


Fig. 2. W-0.1% carbon (0.021%), C as analysed; etched in KOH-K₃Fe(CN)₆ (1:1000).

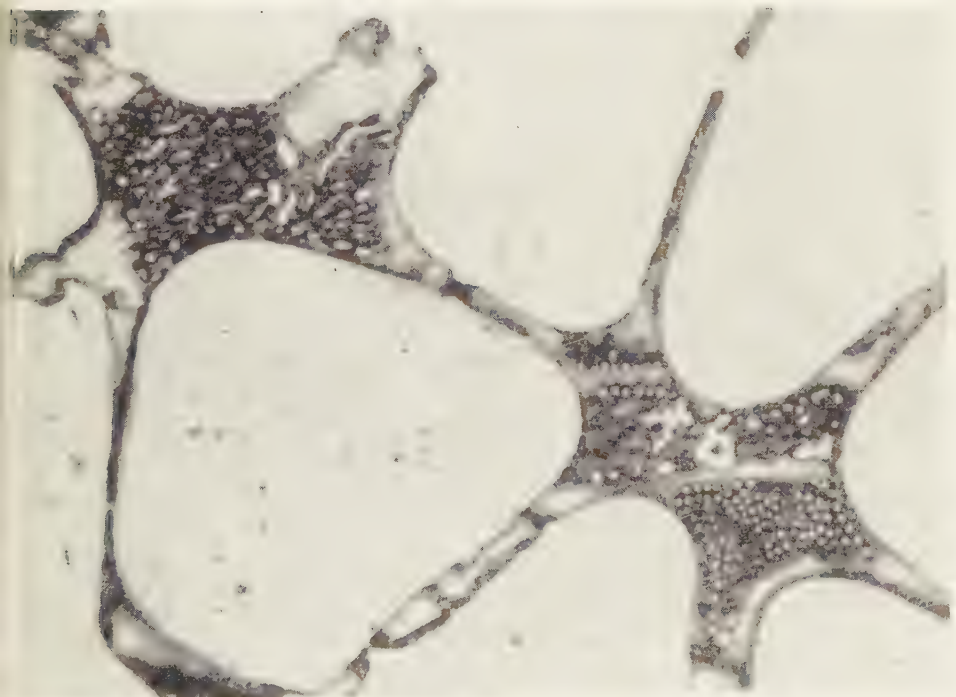


Fig. 3. W-0.1% boron, etched in KOH-K₃Fe(CN)₆ (1:1200).

properties of tungsten. The specimen with 0.1% Al had to be discarded because of its cracks. Beryllium appears to have no effect. Titanium, zirconium, vanadium and chromium, whose solubility in tungsten is relatively high, decrease the density of sintered tungsten with increasing concentration. Although an increase in hardness would be expected with the addition of such elements, as observed in the systems W-Ta¹² and W-Nb^{12,13}, the drop in density causes a detrimental effect. It can be seen that with decreasing solubility of these elements in tungsten (V¹³ and Cr¹⁴ are completely soluble, Ti¹⁵ is soluble up to 25 atomic %, Zr¹⁶ up to 6 atomic %), the density at an alloy addition of 1.0% decreases also. This is apparently due to the

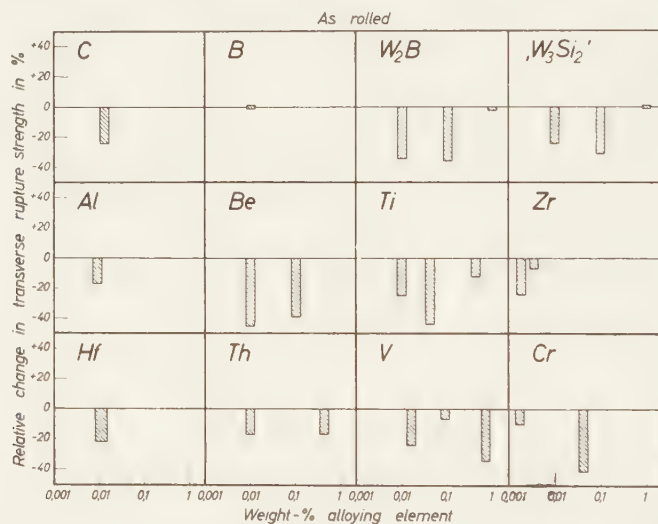


Fig. 4. Influence of alloying on the strength of tungsten (as-rolled).

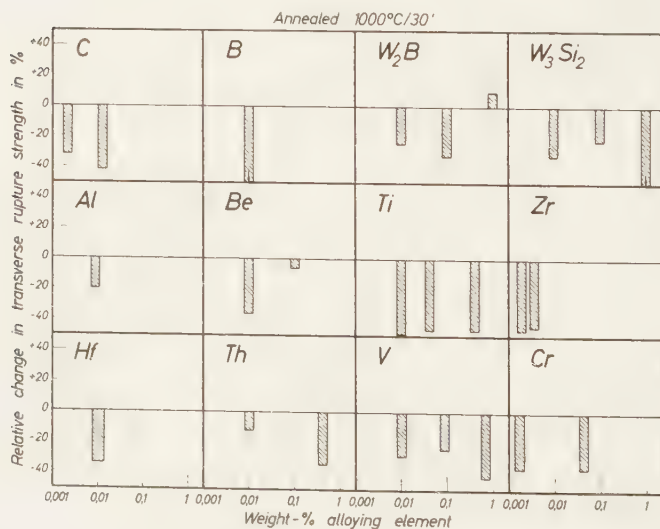


Fig. 5. Influence of alloying on the strength of tungsten (annealed 30 min at 1,000°C)

ferences in diffusivity as explained by the Smigelskas-Kirkendall effect. Hafnium and thorium, having low solubilities¹⁷ in tungsten and forming the most stable oxides during deoxidation of the tungsten, do not influence the density of the compacts at all. The higher hardness met in samples with 1.0% hafnium or thorium added is due to the dispersion of HfO_2 and ThO_2 respectively.

Reliability

A one-pass reduction of approximately 43% was considered sufficient to yield a material satisfactory for preliminary information on the strength and ductility of the

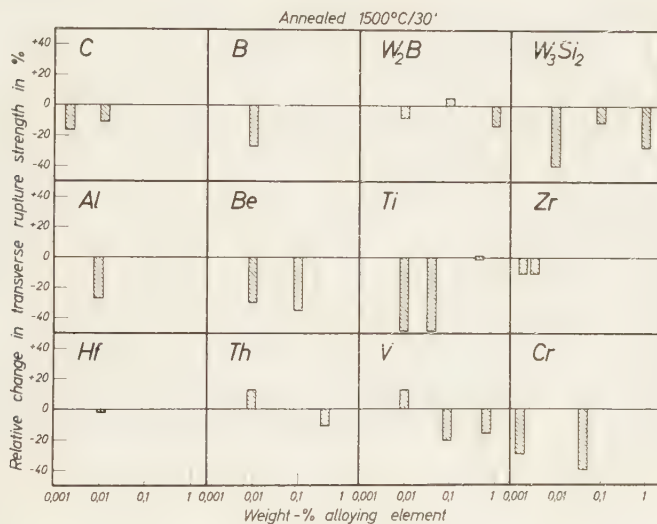


Fig. 6. Influence of alloying on the strength of tungsten (annealed 30 min at 1,500°C).

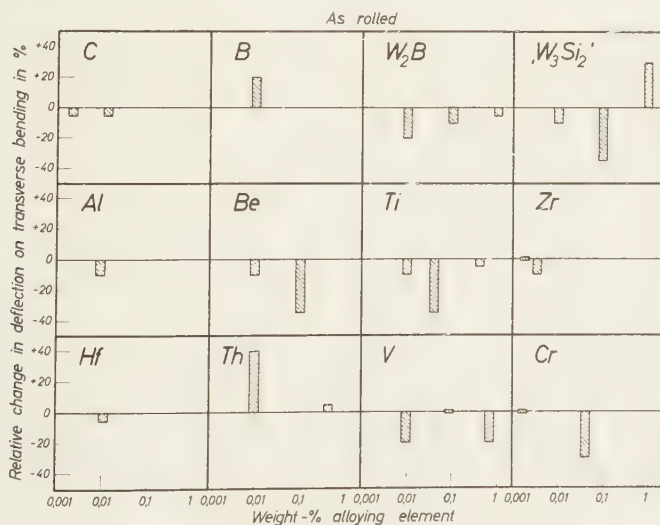


Fig. 7. Influence of alloying on the ductility of tungsten (as-rolled).

tungsten alloys. The rolling of the sintered specimens was carried out at 1,600°C, a temperature high enough to ensure optimum working conditions.

With the exception of the alloy with 0.1% boron which showed severe side-cracking, the alloys appeared to behave similarly to pure tungsten. However, pickling of the rolled specimens was neglected, and this might have yielded more information about the outer appearance of the alloys.

Mechanical properties of alloyed tungsten

The hardness and the strength and ductility of alloyed tungsten as evaluated from

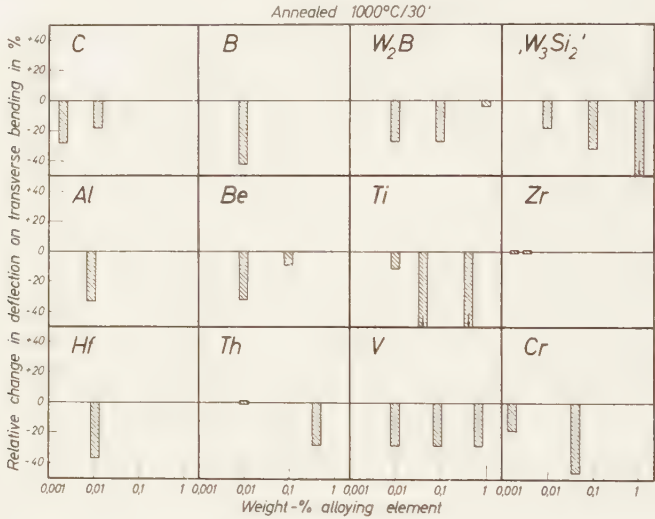


Fig. 8. Influence of alloying on the ductility of tungsten (annealed 30 min at 1,000°C).

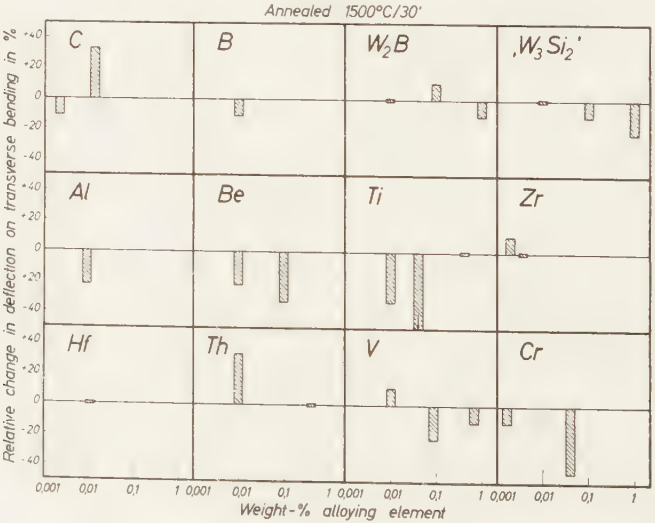


Fig. 9. Influence of alloying on the ductility of tungsten (annealed 30 min at 1,500°C).

pro-transverse bending data are summarized in Table IV and in Figs. 4-9 respectively. The data are rather limited and somewhat scattered so that a detailed discussion is not possible. However, some general observations can be made: 1% W_2B added to tungsten yields a material which is equivalent to pure tungsten and even shows a slight improvement in strength in the annealed condition. Elemental boron



10. W-0.01% thorium, rolled 47% and annealed 30 min at 1,500°C, etched in KOH- $K_3Fe(CN)_6$. ($\times 200$)



11. W-0.1% carbon (0.021% C as analysed), rolled 47% and annealed 30 min at 1,500°C, etched in KOH- $K_3Fe(CN)_6$. ($\times 200$)

TABLE IV
HARDNESS, TRANSVERSE RUPTURE STRENGTH AND DEFLECTION OF TUNGSTEN CONTAINING 0.01-1.0 WEIGHT % OF VARIOUS ALLOYING ELEMENTS

Alloying element	content (%)	VHN (10 kg load) (kg/mm ²)		Transverse rupture strength (kg/mm ²)		Deflection (mm)	
		as-rolled	1,000°/30'	as-rolled	1,000°/30'	as-rolled	1,000°/30'
Tungsten		512	422	32-41	50-53	0.09-0.11	0.10-0.12
		512	422		37		0.08-0.09
	0.004	462	336	27-36	28-34	0.09-0.10	0.07-0.09
		462	349		31		0.08
C		512	349	27-31	29	0.09-0.10	0.09
	0.021	462	366		33		0.11
		462					
		462					
B		462	488				
	(0.01)*	422	383	—40	23-24	0.12	0.06-0.07
		441	383		27		0.08
		488					
W ₂ B		462	402		not workable		
	(0.1)	462	422	27	35-38	0.08	0.09
	(0.01)				31-34		
		462	462				
	(0.1)	462	349	24-26	25-34	0.09	0.08
		462	349		39		0.10
		462					
	(1.0)	462	422	38-39	55	0.09-0.10	0.09-0.12
		462	422		32		0.08
"W ₃ Si ₂ "		512	336	27-31	26-34	0.08-0.10	0.09
	(0.01)	462	349		22	0.09	0.09
		462					
		462					
	(0.1)	488	383	26-28	31-39	0.06-0.07	0.07-0.08
		488	383		33		0.08
	(1.0)	462	422	41	20	0.13	0.04
		462	422		26-27		0.07
Al		462	383	34	33-40	0.09	0.07-0.08
	0.001	462	383		20-27		0.07
		462					
		462					
Be		462			not workable		
	0.001	488	349	19-22	25-32	0.08-0.10	0.07-0.08
	<0.001	462	349		22-26		0.06-0.07
		488	383				
Ti	<0.001	488	383	22-25	—47	0.06-0.07	0.10
		462	383		22-24		0.06
		462					
		488					
		488	383	22-31	22-25	0.08-0.10	0.06-0.10
	0.01				16-19		0.05-0.06

Zr	0.065	462 462 488	512 512 462	383 383 383	17-23	24-27	17-19	0.00-0.07	0.06	0.04
	0.64	488 488	462 462	383 383	35-36	24-27	30-37	0.09-0.10	0.05-0.07	-0.08-0.09
	traces	488 488	462 462	422 441	29-31	20-27	25-33	0.08-0.11	0.07-0.11	0.07-0.10
	0.006	488 488	422 422	462 422	33-38	28	22-32	0.08-0.10	0.11	0.09
Hf	0.70 (0.01)	462 462	462 462	422 422	29-32	not workable 26-34	29	0.08-0.09	0.06-0.08	0.06-0.07
	0.015	462 462	462 462	422 422	30-32	31-34	36	0.09-0.10	0.06-0.07	0.09
	0.26 (0.01)	462 462	462 462	462 462	22-34	not workable 28-34	27-29	0.08-0.10	0.08-0.10	0.08-0.09
	0.01	422 422 488	462 462 462	422 422 336	27-36	30-44	38-42	0.10-0.14(!)	0.10-0.12	0.10-0.1
V	0.65	422 422	462 462	462 462	29-36	29-34	32-33	0.10-0.11	0.08	0.08-0.09
	0.01	488 488	488 488	422 422	30-31	34-36	38-48	0.08	0.08	0.09-0.10
	0.095	488 462	462 462	383 349	38	27-38	24-29	0.10	0.07-0.08	0.07
	0.85	462 488 488	512 488 488	349 462 462	26-27	26-29	30-31	0.08	0.08	0.07-0.08
Cr	0.0028	512 512	512 488	349 349	37	31-32	22-26	0.10	0.08-0.10	0.08
	0.066	462 462 488	488 488 488	388 462 441	24	31	22	0.07	0.06	0.06
	0.55	488	488	441	not workable					

* not analysed. Value in () refers to weighed-in concentrations.

and tungsten silicide, which lead to good strength in the as-rolled condition, have a detrimental effect after annealing at 1,000 and 1,500°C. Carbon, aluminium, beryllium, vanadium and chromium have no positive influence on the strength of tungsten. Additions of 1%, titanium and small amounts of zirconium, hafnium and thorium tend to increase the strength of the recrystallized material.

Considering now the ductility of tungsten, as measured by deflection on transverse bending, three categories of effects can be distinguished.

1. Boron and silicon, added as 0.01% W_2B and " W_3Si_2 ", respectively, have no adverse effect on the ductility of recrystallized material. Purification of tungsten through evaporation of BO_3 and SiO does not *improve* the ductility, and yields only average materials.

2. Vanadium, chromium and small additions of aluminium, beryllium, and titanium decrease the ductility of the recrystallized material.

3. Zirconium, hafnium and thorium, which produce finely dispersed highly refractory oxides on deoxidation, improve the ductility of the recrystallized material. The maximum effect has been found with the addition of 0.01% Th, which results in a 32% higher ductility of tungsten annealed for 30 min at 1,500°C. Fig. 10 shows a micrograph of this material; no recrystallization has taken place, and a fine grain size has been stabilized throughout the specimen.

The addition of 0.1% carbon has a similar effect on recrystallized tungsten owing to the dispersed carbide phase, as previously shown in Fig. 2. After recrystallization the structure of the worked alloy now containing 0.021% C has large elongated grains with the carbide phase at the grain boundaries, as shown in Fig. 11.

DISCUSSION AND SUMMARY

The results obtained in these preliminary experiments indicate that the improvement of the mechanical properties of tungsten by means of deoxidation during the sintering process requires further investigation. It appears that a distinction must be made between the effects of elements forming (a) volatile oxides, (b) stable refractory oxide dispersions in the tungsten matrix, and (c) solid solutions with tungsten.

Carbon, boron and silicon belong to the first group of elements examined. Comparing the heats of formation of their respective oxides¹⁸, boron should be by far the best deoxidiser in forming B_2O_3 , which will be evaporated quite easily. In fact boron purifies the tungsten to a very high degree, but so far no relation between purity of tungsten and its mechanical properties has been established. Silicon appears to be the least active element among the first group with respect to the mechanical properties of tungsten, although its purifying effect is considerable.

Aluminium, beryllium, zirconium, hafnium and thorium all form refractory oxides when they are added as deoxidizers. ThO_2 , which has the highest stability at the sintering temperature, also shows the most pronounced influence on the strength and ductility of tungsten. Zirconium and hafnium might well become equivalently useful in the grain stabilization of tungsten, although ZrO_2 is rather easily reduced by tungsten at high temperatures. Though the stability of Al_2O_3 is high, the comparatively low melting point of this oxide will lead to its reduction and evaporation in form of AlO or some aluminate. Aluminium as a sole additive does not improve the properties of tungsten but leads to detrimental results. Altogether, its use as deoxidiser without

The addition of other substances is not very promising, particularly when its adverse influence on the sintering behaviour is considered.

Tanadium and chromium are among the elements with high solubility in tungsten and give no improvement of its properties.

With regard to titanium, it is doubtful whether the positive influence of 1.0% Ti on ductility is due to the formation of TiO_2 , which has a melting point of only 1,920°C. In earlier experiments¹⁹, a relatively good workability of tungsten was obtained by addition of up to 5% Ti. In restraining recrystallization the action of Ti may be due to the precipitation of titanium carbide, as has been claimed for molybdenum. The effect of titanium should be more closely studied.

The addition of tantalum, niobium, manganese, rhenium and part of the group IVa metals to tungsten is under investigation. Double sintering with intermediate rolling or swaging, and combinations of elements with varying deoxidation effects are among the points of primary interest. These investigations, with the goal of obtaining a polycrystalline sintered tungsten metal having improved strength and ductility are expected to initiate new work in this direction; the potentiality of tungsten as a high-temperature construction material will be greatly increased once its recrystallization behaviour can be controlled.

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EFFECT OF HYDROGEN ON DISLOCATION LOCKING IN NIOBIUM

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SUMMARY

The strain-aging tendencies of as-received commercial purity arc-melted Nb and hydrogenated Nb from the same heat were investigated using yield point return and dynamic modulus measurements to study the aging process. Comparison of activation energies for strain aging with those for interstitial diffusion revealed that hydrogen could be responsible for dislocation locking in niobium.

In order to obtain a measure of the degree of dislocation locking as a function of hydrogen content, the lower yield stress of electron beam melted Nb (both as-received and hydrogen-charged) was measured, as a function of grain diameter, using a constant strain rate and test temperature. In the equation, $\sigma_y = \sigma_t + k_y d^{-1/2}$, the parameter σ_t was found to be relatively insensitive to hydrogen content, and the parameter, k_y , a measure of the locking strength, was found to increase with increasing hydrogen content.

INTRODUCTION

Strain aging due to dislocation locking has been thoroughly investigated in alpha iron and steel using measurements of many properties to study the kinetics of the aging process: hardness¹, yield point return², electrical resistivity^{3,4}, notched bar impact strength⁵, and internal friction^{6,7}. It is well known that carbon and nitrogen can cause dislocation locking in alpha iron, and ROGERS^{8,9} has shown that hydrogen can form pinning atmospheres in iron at low temperatures and in the absence of carbon and nitrogen.

Numerous properties and phenomena in the group 5A and group 6A metals (V, Cb, Ta and Cr, Mo, W) are influenced by or attributed to dislocation — interstitial atom interactions in much the same manner as in alpha iron. The upper and lower yield point effect has been reported for all six elements, as has been the strong temperature dependence of the tensile and yield stresses at low temperatures¹⁰. Delayed yielding and preyield microcreep have been observed in Cb and Ta¹¹ and Mo^{11,12,13}. Peaks in the tensile or yield strength versus temperature curves have been reported for V, Cb, Ta, Cr, and W¹⁰, and the influence of interstitial elements on the ductile-brittle

position of the BCC refractory metals has recently been summarized¹⁴. However, strain-aging studies have yet been made in these materials to show conclusively which interstitial elements are responsible for these observations. Recent treatments regarding the ductile-brittle behaviour of BCC metals has yielded relationships which express the lower yield stress as a function of grain size^{5,16,17}. The expression developed by PETCH¹⁶ is of the form:

$$\sigma_y = \sigma_i + k_y d^{-\frac{1}{2}} \quad (1)$$

where $k_y = \sigma_D l^{\frac{1}{2}}$. The term σ_y is the shear stress for yield propagation (lower yield stress), d is the grain diameter, σ_D is the shear stress to unpin a dislocation from its atmosphere, σ_i is the shear stress resisting the movement of dislocations across the slip plane after they have been unpinned, and l is the distance from piled-up dislocations at the head of a plastic front to the nearest Frank-Read sources. The parameter σ_i can be further divided into a temperature-independent term σ_i^* and a temperature-dependent term σ_0 such that $\sigma_i = \sigma_i^* + \sigma_0$. The σ_i^* term arises from the resistance of random solute atoms, fine precipitates and lattice defects to dislocation movement, and the σ_0 term represents an appreciable Peierls-Nabarro stress. A number of investigations have been made on various BCC metals using this approach: alpha Fe^{18,19}, Nb²⁰, Mo and irradiated Mo^{21,22} and Cr²³.

The experimental work reported here is conveniently broken into two parts, the first being strain-aging studies on Nb to determine which interstitial element(s) is responsible for dislocation locking, and the second being measurements of the lower yield stress as a function of grain diameter and interstitial content. The interstitial content varied in the latter phase was hydrogen, which was shown to be responsible for the strain-aging behaviour.

TABLE I
CHEMICAL ANALYSES OF MATERIALS. WEIGHT PERCENT

Material	H	C	O	N	Phase of work material used in
As received comm. melted Nb	0.0010	0.005	0.0117	0.0049	Strain aging; yield point return and dynamic modulus
Hydrogen ann. comm. (650°C, 7 h)	0.0779	—	0.0848	0.0546	Strain aging, dynamic modulus
As received electron beam melted Nb	0.0007	0.0104	0.023	0.0215	Yield stress-grain size studies
Electron beam melted Nb, hyd. ann. 300°C, 5 h; argon ann. 300°C, 5 h	0.0015	—	0.0120	0.0100	Yield stress-grain size studies
Electron beam melted Nb, hyd. ann. 300°C, 8 h; argon ann. 300°C, 8 h	0.0061	—	0.0190	0.0090	Yield stress-grain size studies

MATERIAL

Both arc-melted Nb and electron beam-melted Nb were used in this investigation: the former for the strain-aging studies, and the latter for the yield stress-grain size measurements. The commercial purity arc-melted Nb was obtained from Fansteel Metallurgical Corporation in the form of $\frac{1}{2}$ in. diameter rod recrystallized to a fine grain size (about 700 grains/mm²). The composition of the as-received material is shown in Table I. Samples of this material were also hydrogen annealed at 650°C, 7 h for one phase of the dynamic modulus strain-aging studies. Table I shows that this treatment raised the hydrogen content from 10 p.p.m. to 779 p.p.m. The chemical analysis for hydrogen was made on the dynamic-modulus/strain-aging sample aged at 24°C (see Fig. 6), after completion of the test. This increase in hydrogen concentration was sufficient to cause a second phase (presumably Nb hydride) to form throughout the material. Microstructures of the as-received and hydrogen-annealed materials are shown in Figs. 1 and 2, respectively.

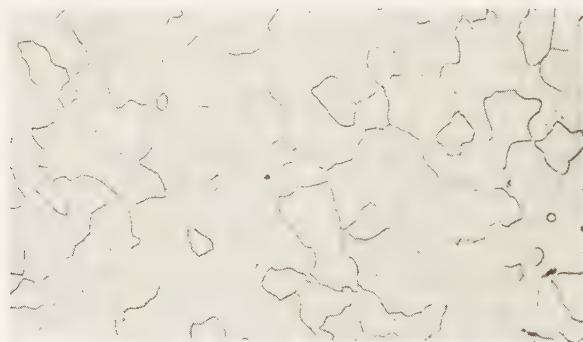


Fig. 1. Microstructure of as-received commercial arc-cast Nb, HF-HNO₃, etch. ($\times 100$)

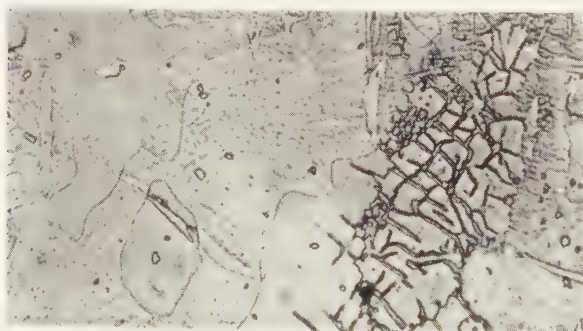


Fig. 2. Microstructure of hydrogenated Nb (650°C, 7 h), showing hydride second phase, HF-HNO₃, etch. ($\times 500$)

The electron beam-melted Nb was supplied by Mallory Sharon Metals Corporation in the form of $\frac{1}{2}$ in. diameter recrystallized rod. The recrystallization anneals used to obtain the various grain sizes are as follows: 0.0090 cm, 1 h at 1,125°C; 0.0426 cm, 1 h at 1,300°C; 0.0920 cm, 3 h at 1,400°C. Samples of each grain size were tested under each of three conditions, as-received and two conditions of hydrogen annealing. T

hydrogenating treatments, together with the resulting chemical compositions are given in Table I. Hydrogen charging was performed on the $\frac{1}{2}$ in. diameter rod, prior to machining the tensile samples. Following hydrogen annealing, and also prior to machining, samples were argon-annealed as described in Table I, in order to flatten out concentration gradients. Chemical analyses on hydrogen-charged material were made on specimens 0.215 in. diam. and 2 in. long prepared to have compositions representative of the gauge-section of the tensile samples.

EXPERIMENTAL PROCEDURE

Use of yield point return and dynamic modulus measurements to study the strain-aging process have previously been shown to be reproducible techniques. Both methods were used to study the strain aging of columbium in order to validate the results more thoroughly.

Strain aging - yield point return

Tensile samples of arc-melted Nb were machined with threaded ends and were 1 in. long with a 1 in. gauge length and a gauge diameter of 0.215 in. A "hard" twin-Emery SR-4 Tensile Testing Machine, Model FGT, was used for tensile straining, load-strain curves being autographically recorded. All testing in this phase was done at -50°C and a strain rate of 0.005 min^{-1} . The low test temperature not only promoted the yield drop, but also minimized interstitial diffusion during testing and saving the time it took to transfer samples to the aging furnace. The temperature control in this furnace was $\pm 2^{\circ}\text{C}$.

Initial plastic straining of specimens to about 1% strain resulted in the characteristic upper and lower yield point, the upper yield point being that stress required

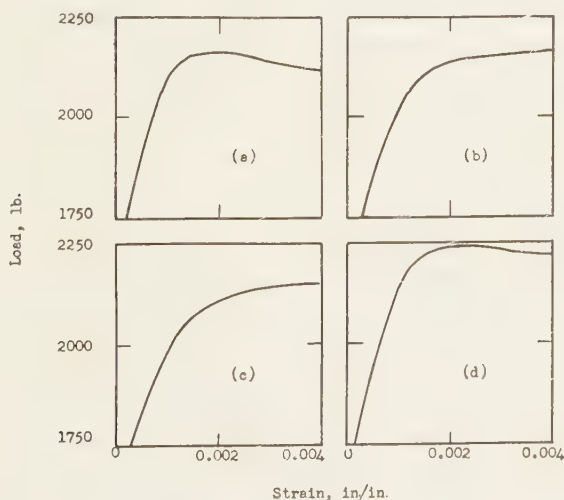


Fig. 3. Load-strain curves for one sample of commercial arc-melted Nb, tested at -50°C and a strain rate of 0.005 min^{-1} . Critical aging time taken as 4 min.

- | | |
|---|---|
| (a) Initial loading | (b) Immediate reloading |
| $D_0 = 0.2152 \text{ in.}$ | $D_0 = 0.2125 \text{ in.}$ |
| (c) Aged 260°C , 3 min. | (d) Aged 260°C , 4 min. |
| $D_0 = 0.2123 \text{ in.}$ | $D_0 = 0.2120 \text{ in.}$ |

to break an "avalanche" of dislocations free from their pinning atmospheres, and the lower yield point being the stress required to maintain the motion of the dislocations in their slip planes once they had been torn free. Immediate reloading produced no yield drop, but aging for a sufficient length of time at a given temperature caused the yield point to return. A load drop of approximately 20 pounds (about 550 p.s.i.) was arbitrarily selected as being evidence of the yield point return. Fig. 3 illustrates a typical series of load-strain curves in the region of the yield point for a sample aged at 260°C.

Deformed samples were aged from 121–260°C. The critical times of aging to cause yield point return found to be: 121°C, 145 min; 149°C, 50 min; 204°C, 12 min; and 260°C, 4 min. The temperature dependence of the yield point return rate was found to be adequately expressed by an Arrhenius type of rate equation:

$$\text{rate} = Ae^{-Q/RT} \quad (2)$$

where A is the frequency factor, Q the activation energy, R the gas constant and T the absolute temperature. The data are plotted in Fig. 4, and the activation energy for strain aging calculated from the slope was found to be 10,500 cal/mole. This value is considerably lower than the Q values for diffusion of carbon, oxygen, or nitrogen in Nb (see Table II), but in good agreement with the activation energy of 9,370 cal/mole

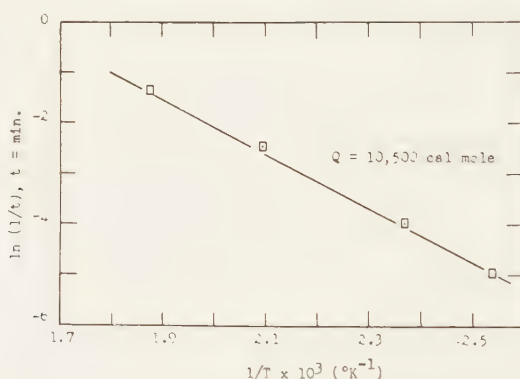


Fig. 4. Yield point return strain-aging data for arc-melted commercial Nb.

TABLE II
SUMMARY OF DIFFUSION DATA FOR INTERSTITIALS IN NIOBIUM

Diffusing element	D_0 (cm ² /sec)	Q (cal/mole)	Reference
Oxygen	0.0147	27,600	ANG ²⁵
Oxygen	0.00407	24,900	KLOPP <i>et al.</i> ²⁶
Oxygen	0.014	26,600	POWERS AND DOYLE ²⁷
Oxygen	—	22,000	MARX <i>et al.</i> ²⁸
Nitrogen	0.0098	38,600	ANG ²⁵
Nitrogen	0.0072	34,800	POWERS AND DOYLE ²⁹
Nitrogen	0.061	38,800	ALBRECHT AND GOODE ³⁰
Nitrogen	—	35,700	MARX <i>et al.</i> ²⁸
Carbon	0.0046	33,000	POWERS AND DOYLE ²⁹
Carbon	0.015	27,000	WERT ³¹
Hydrogen	0.0215	9,370	ALBRECHT <i>et al.</i> ²⁴

given by ALBRECHT *et al.*²⁴ for hydrogen diffusion in Nb. It is therefore reasonable to conclude that hydrogen is responsible for strain aging in niobium.

Strain aging - dynamic modulus

Dynamic moduli of as-received and hydrogen-annealed arc-melted Nb were determined from resonant frequency measurements using a free-free beam technique. A transverse sonic wave was propagated the length of a sample, having nominal dimensions of 3 in. $\times$ $\frac{1}{2}$ in. $\times$ $\frac{1}{4}$ in., the $\frac{1}{4}$ in. dimension being in the plane of vibration. All resonant frequency measurements were made at room temperature, with a control of about $\pm 1^\circ\text{C}$.

The following equation was used to calculate the dynamic modulus of elasticity

$$E = CWF_r^2 \quad (3)$$

where E is the modulus in p.s.i., F_r the resonant frequency in c/sec, W the specimen weight in pounds, and $C = 2.45 \cdot 10^{-2} L^2 T / bt^2$, L , b and t being respectively the length, width, and thickness in inches. The term T is a correction factor given by $T = \varphi(\nu) / (1 + \nu)$, where φ designates a function, ν is Poisson's ratio, and K is the radius of gyration $= 0.289 t$ for a prism. The values of T were determined with the aid of ref. 32. Elastic deformation was achieved by compressing samples in the $\frac{1}{4}$ in. direction, using a head travel rate of 0.005 in./min, *i.e.* approximate strain rate of 0.02 min^{-1} . The as-received Nb was compressed 3%, but the hydrogenated Nb was deformed only 1% since it was noted that the charging treatment caused considerable embrittlement. Modulus determinations were made prior to deformation, E' , immediately after deformation, E_0 , and as a function of aging time at temperature, E_t . Deformation of as-received Nb caused a modulus decrease of about $0.1\text{--}0.3 \cdot 10^6$ p.s.i., this lowering being attributed to the creating of free dislocations both by unpinning locked ones and by generating fresh ones. Aging at temperatures of 24–94°C caused the modulus

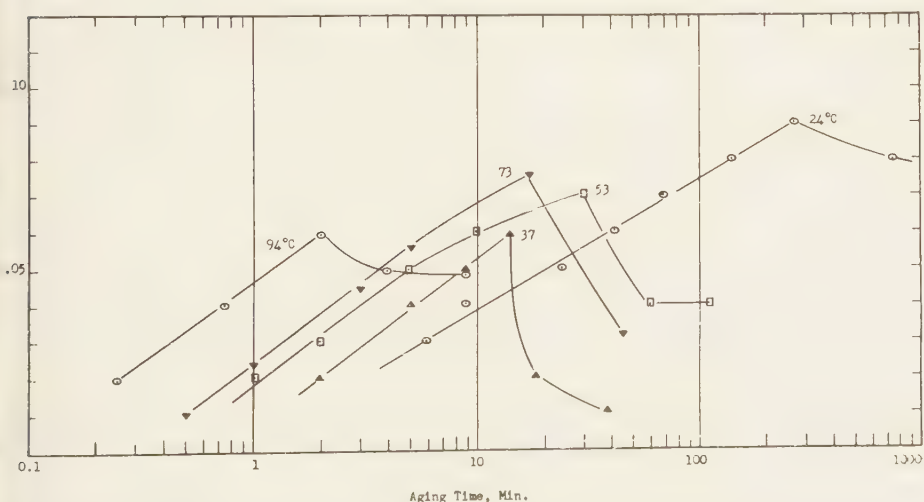


Fig. 5. Recovery of dynamic modulus of as-received commercial Nb as a function of aging time and temperature, after 3% deformation by compression. All modulus measurements at room temperature.

to increase toward the unstrained value, and then decrease after reaching an "aging peak". The modulus recovery, defined as $\Delta E = E_t - E_0$, is shown as a function of aging time and temperature in Fig. 5, for as-received Nb. Values of E' , E_0 , and E_m , the modulus at the aging peak, are listed in Table III.

TABLE III
DATA FOR COMMERCIAL NIOBIUM, AND HYDROGENATED NIOBIUM, SHOWING THE EFFECTS OF DEFORMATION AND SUBSEQUENT AGING ON THE DYNAMIC MODULUS
All modulus measurements made at room temperature

Material	E' , mod. of undeformed spec. (10^8 p.s.i.)	E_0 , mod. immed. after deformation (10^8 p.s.i.)	E_m , Max. re-covered mod. (at aging peak) (10^8 p.s.i.)	Aging temp., °C
Comm. Nb	15.861	15.764	15.854	24
Comm. Nb	16.053	15.960	16.092	37
Comm. Nb	15.997	15.727	15.798	53
Comm. Nb	16.002	15.878	15.954	73
Comm. Nb	15.935	15.638	15.697	94
Hydrogenated Nb	13.839	15.024	15.949	24
Hydrogenated Nb	14.857	15.232	16.234	53
Hydrogenated Nb	15.607	15.100	16.059	73
Hydrogenated Nb	13.446	14.817	16.338	94

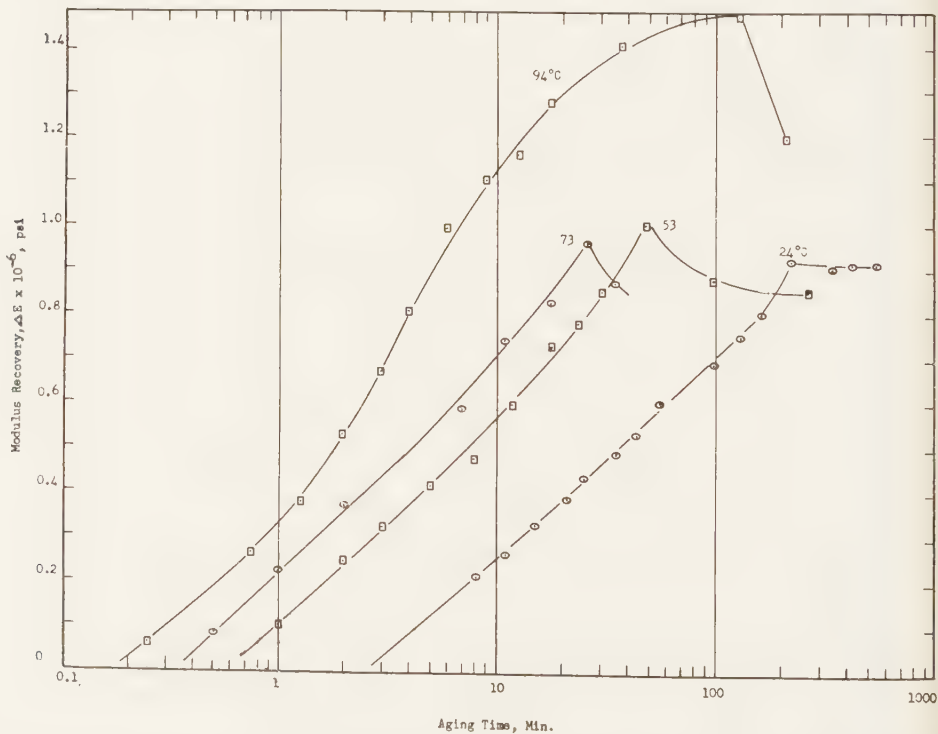


Fig. 6. Recovery of dynamic modulus of hydrogenated Nb (650°C, 7 h) as a function of aging time and temperature, after 2% deformation by compression. All modulus measurements at room temperature.

The effect of deformation on the dynamic modulus of hydrogenated Nb was somewhat irregular, (see Table III), sometimes increasing the modulus above the unstrained value, and other times lowering it. This behaviour is probably associated with the presence of the brittle internal hydride phase. However, the modulus recovery versus aging time curves of this material (Fig. 6) are quite similar to those for the as-received material. It is seen in Figs. 5 and 6 that the maximum modulus recovery values of the hydrogenated material are more than an order of magnitude greater than those of the as-received Nb.

The temperature dependence of the modulus recovery rate can also be expressed in rate equation of the Arrhenius type. Plots at several iso-modulus recovery values are shown in Fig. 7. The activation energies calculated from the slopes of the curves are 7,830–8,280 cal/mole, as-received Nb; and 8,080–9,920 cal/mole, hydrogenated Nb. These values are in good agreement with the activation energy determined from yield point return-strain aging studies, and with the Q value of 9,370 cal/mole for the diffusion of hydrogen in Nb.

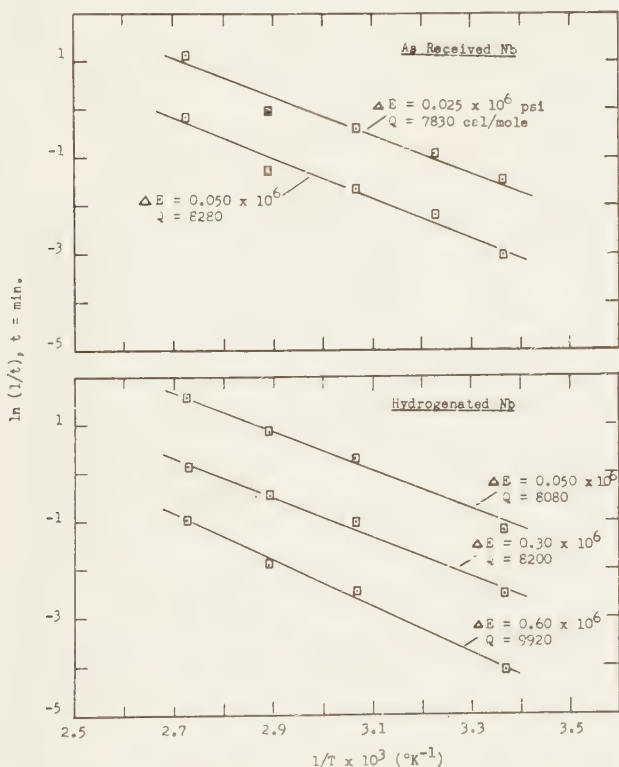


Fig. 7. Dynamic modulus strain-aging data for as-received commercial Nb and hydrogenated Nb.

Lower yield stress measurements

The tensile sample configuration used in this part of the work was the same as that used in the yield point return-strain aging studies. All tensile testing was at 24°C.

and a strain rate of 0.005 min^{-1} , the load strain curves being recorded autographically on the "hard" Baldwin-Emery Tensile Machine. Care was taken to insure axial loading through the use of lubricated spherical seats.

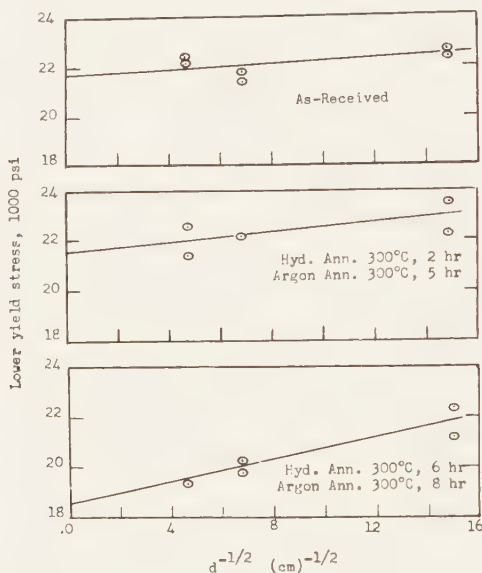


Fig. 8. Variation of lower yield stress of electron beam Nb with grain size and hydrogen content. Tested at 24°C and a strain rate of 0.005 min^{-1} .

In Fig. 8 the lower tensile yield stress is shown as a function of $d^{-1/2}$ for Nb material of three different hydrogen contents, 7, 15, and 61 p.p.m. It is seen that a straight line can be drawn for each of the compositions, and that the slope, $2k_y$, increases with increasing hydrogen content. The slope of the curves is $2k_y$, since tensile stress rather than shear stress values are plotted, *i.e.* to a first approximation the shear stress is half the tensile stress. The lower yield stress extrapolated to $d^{-1/2} = 0$ gives the value of σ_i , and it is noted that this parameter decreases slightly with increasing hydrogen content. The actual yield stress-grain size data is given in Table IV, and the calculated values of k_y and σ_i are shown in Table V, together with the earlier work of ADAMS *et al.*²⁰.

TABLE V

VALUES OF σ_i AND k_y DETERMINED IN THIS WORK FOR AS-RECEIVED AND HYDROGEN-ANNEALED ELECTRON BEAM Nb, COMPARED WITH THE RESULTS OF ADAMS *et al.*²⁰

Hydrogen content (p.p.m.)	Test temp. ($^\circ\text{C}$)	Strain rate (min.^{-1})	σ_i (tensile stress), p.s.i.	σ_i (shear stress) (p.s.i.)	(dyne/cm^2)	$k_y \cdot 10^{-8}$ ($\text{dyne cm}^{-3/2}$)	Reference
7	24	0.005	21,700	10,850	$7.48 \cdot 10^8$	1.72	This work
15	24	0.005	21,500	10,750	$7.41 \cdot 10^8$	3.20	
61	24	0.005	18,600	9,300	$6.41 \cdot 10^8$	7.14	
200	—196	0.012	96,000	48,000	$3.31 \cdot 10^9$	5.18	ADAMS <i>et al.</i> ²⁰
200	—78	0.012	36,000	18,000	$1.24 \cdot 10^9$	3.80	
200	20	0.012	20,000	10,000	$6.90 \cdot 10^8$	2.76	
200	—196	3.70	113,000	56,500	$3.90 \cdot 10^9$	7.25	

All tests at 24°C and a strain rate of 0.005 min⁻¹

Recrystallization treatment	Grain diameter ($\pm d$), μ m	$d^{-1/2}$ ($\text{cm}^{-1/2}$)	Lower tensile yield stress (p.s.i.)	Hydrogenating treatment	Composition			
					H	C	O	N
1,125°C, 1 h	0.0090	14.90	24,070	As-received	0.0007	0.0104	0.023	0.0215
1,125°C, 1 h	0.0090	14.90	22,300	"	0.0007	0.0104	0.023	0.0215
1,300°C, 1 h	0.0426	6.85	21,460	"	0.0007	0.0104	0.023	0.0215
1,300°C, 1 h	0.0426	6.85	21,630	"	0.0007	0.0104	0.023	0.0215
1,400°C, 3 h	0.0920	4.66	22,380	"	0.0007	0.0104	0.023	0.0215
1,400°C, 3 h	0.0920	4.66	22,340	"	0.0007	0.0104	0.023	0.0215
1,125°C, 1 h	0.0090	14.90	22,110	300°C, 2 h hyd. 300°C, 5 h argon	0.0015	—	0.012	0.010
1,125°C, 1 h	0.0090	14.90	23,660	"	0.0015	—	0.012	0.010
1,300°C, 1 h	0.0426	6.85	22,290	"	0.0015	—	0.012	0.010
1,400°C, 3 h	0.0920	4.66	22,670	"	0.0015	—	0.012	0.010
1,400°C, 3 h	0.0920	4.66	21,450	"	0.0015	—	0.012	0.010
1,125°C, 1 h	0.0090	14.90	22,380	300°C, 6 h hyd. 300°C, 8 h argon	0.0061	—	0.019	0.009
1,125°C, 1 h	0.0090	14.90	21,010	"	0.0061	—	0.019	0.009
1,300°C, 1 h	0.0426	6.85	19,690	"	0.0061	—	0.019	0.009
1,300°C, 1 h	0.0426	5.85	20,290	"	0.0061	—	0.019	0.009
1,400°C, 3 h	0.0920	4.66	19,305	"	0.0061	—	0.019	0.009

DISCUSSION

Strain aging

The agreement between activation energies for strain aging and the activation energy for the diffusion of H in Nb is good evidence that this interstitial element can cause dislocation locking. This conclusion is not unexpected, since it has been shown that hydrogen can markedly affect the mechanical properties of another Group 5A refractory metal, vanadium³³.

An interesting feature in the dynamic modulus-strain aging studies is that for both materials, the modulus recovery versus aging time curves exhibited maximums or aging peaks. This characteristic can be explained in terms of an "overaging" effect. THOMAS AND LEAK⁷ have shown from internal friction strain aging studies on alpha-iron that more carbon or nitrogen atoms are attracted to dislocations during strain aging than can be retained in local solid solution. This results in the formation of a fine coherent precipitate in the region of the dislocation stress field. If these precipitates contribute to dislocation pinning, then the aging peaks may possibly be due to their coalescence as a result of overaging.

Lower yield stress

The values of σ_i and k_y shown in Table V were determined for conditions of $T = 24^\circ\text{C}$, and $\dot{\epsilon} = 0.005 \text{ min}^{-1}$. This data is in good agreement with the room temperature results of ADAMS *et al.*²⁰. These workers have shown that k_y increases with increasing strain rate and decreasing temperature at constant composition. These studies have revealed that k_y increases with increasing hydrogen content at constant test temperature and strain rate. The value of k_y is increased more than fourfold by raising the hydrogen content from 7 p.p.m. to 61 p.p.m. The term k_y equals $\sigma_D l^{\frac{1}{2}}$, and hence is a measure of the locking strength. The increase in k_y with increasing hydrogen content therefore logically arises from an increase in σ_D , the shear stress required to unpin a dislocation from its atmosphere.

ADAMS has shown that σ_i increases with decreasing temperature and increasing strain rate. It is seen in Table V that σ_i decreases slightly with increasing hydrogen content, but the degree of lowering may well be within the limits of experimental error. The temperature-dependent portion of σ_i could not cause a variance of σ_i in these tests since all yield stress measurements were at constant temperature. The temperature-independent portion, σ_i^* , is apparently unaffected, or possibly slightly decreased by increasing the hydrogen content. At any rate, it can be concluded that increasing the hydrogen content (to 61 p.p.m.) does not cause an increased resistance to the motion of dislocations once they have been broken free from their pinning atmosphere. It remains to be seen whether or not hydrogen charging to the extent of forming an internal hydride phase has any effect on the parameters k_y and σ_i .

CONCLUSIONS

Yield point return and dynamic modulus measurements have been used to study the strain aging of commercial purity arc-melted niobium. Evaluation of the temperature dependence of the strain-aging rate revealed an activation energy which was in good agreement with the activation energy for the diffusion of hydrogen in Nb. It is therefore concluded that hydrogen can be responsible for dislocation locking in niobium.

Results from lower yield stress-grain size investigations on electron beam Nb revealed that the parameter k_y , a measure of the locking strength, increases with increasing hydrogen content. The fact that the parameter σ_i is relatively unaffected by hydrogen content indicates that the amount of hydrogen in solution does not have a significant effect on the resistance to the motion of dislocations in their slip planes, once they have been broken free from their pinning atmospheres.

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VI. Refractory Metals — What of the Future?

UNITED STATES AIR FORCE PROGRESS REPORT ON REFRACTORY METALS

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SUMMARY

A cross-section of the research and development activities of the U.S. Air Force in the refractory metals area is presented. Emphasis is being placed on the development of high-strength alloys for structural applications at temperatures in excess of $1,100^{\circ}\text{C}$. Studies of the oxidation behaviour of tantalum and tungsten are being conducted concurrently with research into protective coatings. A refractory metals processing facility has been established and limited programmes have been conducted on the primary breakdown of arc-cast tungsten and molybdenum base alloys by extrusion.

Starting with the classic Carnot engine, history has shown that one of the conditions an engine must attain to approach maximum efficiency is to achieve a very high intake or operating temperature. Through the years the temperatures at which materials must operate have increased progressively and there are cases where designs have been compromised to permit the use of conventional materials at lower operating temperatures. So whether we are discussing turbines for electric power generation, nuclear reactors, or hypersonic military vehicles, the refractory metals have come of age through necessity. To utilize effectively their potential strength is a formidable problem since nature has imparted many undesirable qualities to these metals: poor oxidation resistance, high density, and brittleness. The United States Air Force has a broad programme on refractory metals designed to utilize these metals in structural applications by solving or lessening the problems associated with them. Since it is beyond the scope of this paper to consider the entire programme, it would be appropriate to present some interesting highlights to convey a representative cross-section of our research and development activities.

As mentioned previously, we are constantly seeking higher temperatures, which in many cases involve an oxidizing environment. The effect of this type of service condition on refractory metals is so severe that the availability of coatings will to a large extent determine the ultimate use of these metals. Since tungsten and tantalum base alloys look promising on a strength-to-weight basis for application at temperatures above $1,400^{\circ}\text{C}$, there is great concern about their oxidation behaviour. As an example of U.S. Air Force sponsored research in this area, let us consider the results so far

obtained on a study of tungsten oxidation¹. This programme has determined that the oxidation behaviour of pure tungsten is influenced by variations of temperature and pressure of oxygen in the temperature range 1,000°C–1,300°C. At 1,200°C and higher, and at an oxygen pressure of 0.01 atmospheres, no measureable oxide pickup is noted. At these temperatures, the oxide evaporates as fast as it is formed, and the oxidation rate is limited by the access of oxygen to the surface. The principal oxide found up to 1,200°C was WO₃. The mechanism of oxidation at 1,200°C and higher is believed to be similar to the combustion of carbon. From this programme it was concluded that the poor protective properties of the oxide scale on tungsten can be attributed to the following factors:

- (1) rapid oxidation reaction,
- (2) poor adherence of the oxide to the metal,
- (3) volatility of the tungsten oxides.

This is not a very bright picture for any proposed structural use of tungsten at high temperatures in the earth's atmosphere. However, work is concurrently being accomplished on the feasibility of utilizing existing technology in the application of tungsten as a leading edge material in hypersonic vehicles². Tensile tests were made on forged

TABLE I
MECHANICAL PROPERTIES FORGED TUNGSTEN BAR*

Sample conditions	Test temp. (°C)	Ultimate tensile strength (p.s.i.)	Tensile yield 0.2% offset (p.s.i.)	% Elongation in 0.8 in.	% Reduction of area
Uncoated	20	162,410	117,740	0	0
Exposed in air		174,590	N.R.	0	0
air argon	1,093	36,970	32,840	16.0	92.5
mixture	1,371	29,600	28,400	10.7	56.9
		34,400	32,100	13.5	96.5
Chrome plated	R.T.	61,900	F.T.	F.T.	F.T.
Exposed in air	1,093	29,200	27,100	F.T.	F.T.
		39,700	N.R.	12.5	58.0
	1,371	32,700	30,600	9.9	55.0
		32,600	30,400	16.0	48.5
Chrome and rhodium plated	20	44,200	N.Y.	0	0
Exposed in air	1,093	28,800	24,700	10.0	9.0
		39,000	N.Y.	20.0	65.9
	1,371	32,400	31,600	6.0	58.0
		33,900	32,500	17.9	76.5
Modified W-2	20	14,860	N.Y.	0	0
0.0052 inch thickness	1,093	8,800	N.Y.	0	0
Exposed in air		37,577	N.R.	18.8	74.0
		37,400	N.R.	17.5	63.0
	1,371	31,400	30,100	17.7	95.3
		30,600	29,900	18.0	96.3

N.R. – Not recorded

F.T. – Failed in threads

N.Y. – No yield

* Prior to testing, the specimens were maintained at the test temperature for 30 minutes.

tungsten test bars coated with readily available materials. The results of this work and the test conditions are shown in Table I.

This work has illustrated the magnitude of the problem of protecting tungsten for none of the coatings was of practical value.

Any future use of tantalum base alloys will likewise involve oxidation problems and consequent use of coatings for various oxidizing environments. A study is being sponsored by the U.S. Air Force on tantalum and its alloys which involves some work on oxidation³. Thus far it has been determined that the tantalum-oxygen and the tantalum-air reactions are quite similar. For both reactions an outer white scale of pure Ta_2O_5 and an inner dark scale of Ta_2O_5 plus traces of Ta_2O_3 were found. The initial reaction follows a parabolic growth law and subsequently this becomes linear after various times depending on the reaction temperature. Above $800^\circ C$ the initial parabolic reaction is extremely short and therefore cannot be detected in air. The reaction rate is believed to be controlled by diffusion of oxygen ions through the adherent dark scale. At temperatures of $1,000$ – $1,200^\circ C$ there is evidence of some sintering of the porous outer white scale.

Attempts have been made to improve the oxidation resistance of tantalum through alloying. Air oxidation rates by continuous weighing techniques have been determined on various alloys up to $1,400^\circ C$. Preliminary results on the most promising alloys are shown in Table II.

TABLE II
AIR OXIDATION RATES OF TANTALUM ALLOYS AT $1,400^\circ C$

Nominal composition weight percent	Weight gain after indicated time (mg/cm ²)			
	1 h	2 h	3 h	4 h
100 Ta*	—	—	—	—
Ta-20 Ti	63.5	96.4	111.6	—
Ta-40 Ti	47.0	78.0	100.0	—
Ta-10 Hf	116.9	—	—	—
Ta-20 Hf	70.1	94.5	106.1	—
Ta-40 Zr	57.4	68.3	73.6	77.7
Ta-10 V-20 Ti	67.4	99.0	—	—

* Oxidized too fast to record

From this data it can readily be seen that some improvement in oxidation resistance through alloying can be attained. This is not the solution to the problem, and research is currently being carried out on coatings for tantalum. At the present time we do not have an acceptable coating for tantalum and its alloys.

Next to oxidation resistance the most important parameter for judging the usefulness of refractory metals is elevated temperature strength. Since many of the more immediate applications of refractory metals require short time exposure to high temperatures, the criterion used for comparison will be ultimate tensile strength at service temperatures.

Refractory metal alloys may be conveniently classified into two types with respect to their mechanical properties:

- (1) high-strength alloys
- (2) oxidation-resistant alloys

The high-strength alloys are those of Mo and W base having small additions of strong carbide formers, *e.g.* Mo-0.5% Ti-0.07% Zr-0.020% C, and columbium and tantalum base having solid solution additions of molybdenum, tungsten, vanadium, niobium and zirconium. Recent work has explored the use of solid solutions of tungsten and molybdenum containing the same type of carbide-forming additions as the molybdenum and tungsten base materials⁴.

The oxidation-resistant alloys are those having columbium or tantalum as a base and additions of titanium up to 10 wt. %³. Other elements are added for solid solution strengthening effects, principally tungsten, molybdenum and vanadium. These alloys have significantly lower strengths than the "high-strength" alloys. A comparison of the strengths of the two classes is given in Table III.

TABLE III

<i>Alloy (w/o)</i>	<i>Type</i>	<i>Condition</i>	<i>Test temp. (°C)</i>	<i>Ultimate tensile strength (p.s.i.)</i>
-2% ThO ₂ ⁷	High strength	Swaged 55% at 1,680°C and stress relieved 30 min at 1,550°C	1,480	33,000
-0.38 TaC ⁷	High strength	Same as above	1,480	42,900
+ 25.1% W ⁴ + 0.11% Zr-0.015% C	High strength	Stress relieved 1 h at 810°C	1,310	73,500
-15% W-5% Mo ¹² + 1% Zr-0.08% C	High strength	Swaged 75%	1,310	32,000
-15% W-5% Mo ¹² + 11% Zr-5% Ti-0.08 C	Oxidation resistant	Swaged 75%	1,310	22,000
-10 Mo-10 Ti ¹³	Oxidation resistant	As-extruded	1,310	19,500

Most of the strengthening mechanisms familiar to the metallurgist have been applied to the refractory metals:

- (1) solid solution strengthening
- (2) dispersion hardening
- (3) precipitation hardening
- (4) strain hardening.

Of these, the first has been most widely applied to columbium and tantalum. It is interesting to note that the element which does most to increase the oxidation resistance, titanium, has the most undesirable effect on the high temperature mechanical properties, *i.e.* the addition of titanium to tantalum and columbium above 10 wt. % lowers the strength of the alloys at 1,090°C^{3,6}.

Dispersion hardening has been applied with marked success to tungsten base alloys⁷. Additions of TaC and ThO₂ to tungsten have increased the strength twofold above that of the base metal at 1,500°C, as well as raising the recrystallization range. Recent investigations on columbium base alloys containing Group IVA additions have indicated that finely dispersed thoria, hafnia, and zirconia may be significant strengthening agents in these alloys⁸.

There have been indications that in the case of molybdenum base alloys and some of the more highly alloyed columbium base materials, dispersed complex carbides are potent strengtheners⁹. Research now under way is exploring the possibility of altering the carbide dispersions by heat treatments coupled with mechanical working to produce desired combinations of high elevated temperature tensile strength and reasonable ductility. It is also believed that suitable heat treatments can enhance the "long-term" mechanical properties, *i.e.* rupture life, at temperatures somewhat lower than those required for aircraft structural applications but in the anticipated operating temperature range (1,100°C) of reactor components for space vehicles.

Strain hardening is of course, employed to strengthen further all refractory metal alloys. However, alloys of columbium and tantalum show a much smaller decrement in tensile strength with the onset of recrystallization than do molybdenum and tungsten alloys^{3,4,5,7}. This fact has led to emphasis on the development of molybdenum and tungsten base alloys with recrystallization temperature ranges well in excess of projected service temperatures, while a similar degree of emphasis was not placed on this type of development in tantalum and columbium alloy research. It has also been shown that an applied stress accelerates the recrystallization process¹⁰, thus underscoring the necessity for molybdenum and tungsten alloys with high recrystallization ranges. The highest recrystallization temperatures obtained to date for molybdenum and tungsten base alloys are presented in Table IV. A comparison of strengths of alloys hardened in each of the above manners is given in Table III.

TABLE IV

<i>Alloy</i>	<i>Condition</i>	<i>Temp. for 100% recryst. in 1 h</i>
W-0.38% TaC	swaged 55% at 1,680°C	2,000°C
Mo-1.27% Ti-0.29% Zr 0.30% C	rolled 75% at 1,310°C	1,760°C

It has been gratifying and helpful to find that much of the information gained in previous work on columbium alloy development concerning the effect of various additions on ultimate tensile strength and oxidation resistance has been directly applicable to the more recent studies on tantalum base alloys. It is found that titanium has the same qualitative effect on the oxidation resistance of columbium as it does on tantalum. Also elements which have proved to be potent strengtheners of columbium, *i.e.* tungsten, molybdenum, hafnium, vanadium, have been shown to have similar strengthening effects on tantalum^{3,5}.

Future research is directed toward development of columbium base alloys for use as structural materials in the range of 1,100°C to 1,350°C, molybdenum base alloys for use between 1,350°C and 1,650°C, and tantalum and tungsten base alloys for operation at temperatures in excess of 1,650°C.

Once an alloy having promising strength and oxidation resistance has been developed, an additional problem arises in the method of fabrication.

Materials that exhibit high mechanical properties are usually difficult to fabricate. Owing to the as-cast structure and the brittle-to-ductile behaviour of the refractory

metal alloys unique methods must be used to fabricate them. One of the critical stages in the fabrication of the refractory metals is the initial breakdown of the ingot. Generally, extrusion is the only way to avoid excessive loss of metal in the breaking down of the cast structure. In order to facilitate the breakdown of experimental refractory alloys the U.S. Air Force operates its own refractory metals processing facility. Part of this facility is a relatively fast acting (900 in./min) 700 ton extrusion press (Fig. 1).

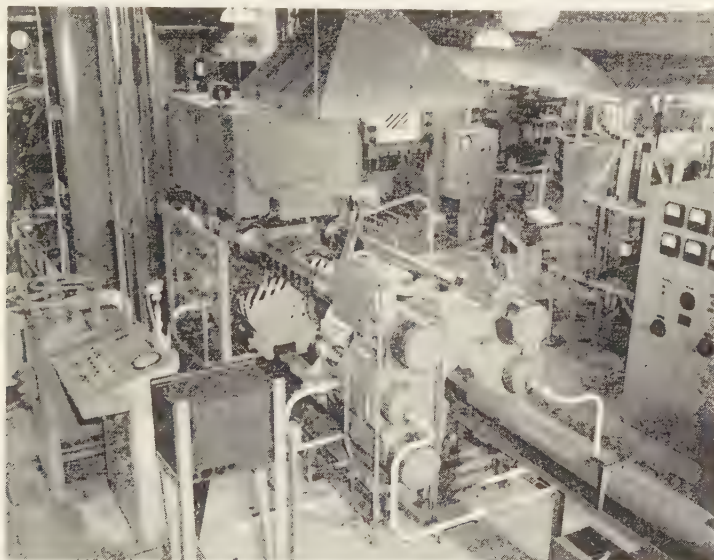


Fig. 1. Extrusion press.

Fast extrusion has a number of advantages:

- (1) the time that the hot billet material is in contact with the die is less than a second;
- (2) the hot billet will not have time to cool off and become more difficult to extrude;
- (3) there is less chance of damage to the container liner;
- (4) the no dwell feature adds an impact force to the billet.

One of the problems in fast extruding is die wash, which is dependent upon such variables as die design, die material, and proper lubricant. At the present time, dies need to hold close tolerances, the principal extruded product being bars which are directly rolled to sheet. The emphasis has been placed on extruding the material rather than producing exacting shapes. One of the main purposes for the extrusion press is to determine the extrudability of newly developed alloys from our alloy development programmes. A typical example is the present effort on experimental molybdenum alloys.

The first major programme that was accomplished on the press was a study to determine whether hot hardness of molybdenum and its alloys could be correlated with extrusion pressure and temperature (Fig. 2).

As Fig. 2 indicates, commercially pure molybdenum, 0.5% Ti-molybdenum, and 45% Ti-0.07% Zr molybdenum were used. It was believed that the extrusion temperature could be predicted by choosing the temperature at which a given value

of hot hardness occurred for each material. After extruding three billets of each alloy it was found that the relationship was not valid. Pressure remained constant over too large an area of the curve to predict accurate extrusion temperatures. However, hot hardness does furnish a rough estimate of extrusion temperature when a molybdenum alloy is being extruded for the first time. It is common practice to heat the billet to a temperature where the hot hardness is below 80 VPH.

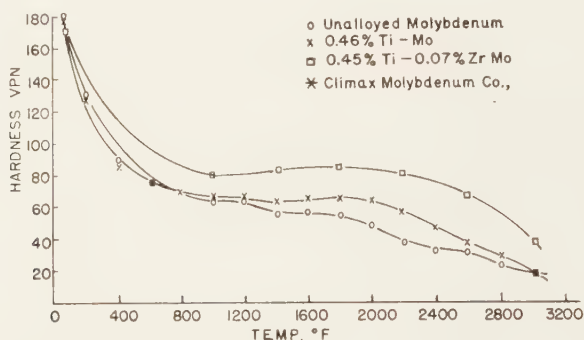


Fig. 2. Hot hardness vs. temperature for molybdenum alloys.

One interesting correlation that did appear was in the weight-percent billet-yield vs. temperature curve for the molybdenum alloys (Fig. 3). The molybdenum alloys appear to have a hot short range at the higher temperatures. The temperatures at which maximum yield was attained for each alloy were:

- (1) 1,090°C for pure Mo, the yield being 73%;
- (2) 1,200°C for 0.5% Ti alloy, the yield being 57%;
- (3) 1,500°C for the TZC alloy, the yield being 62%.

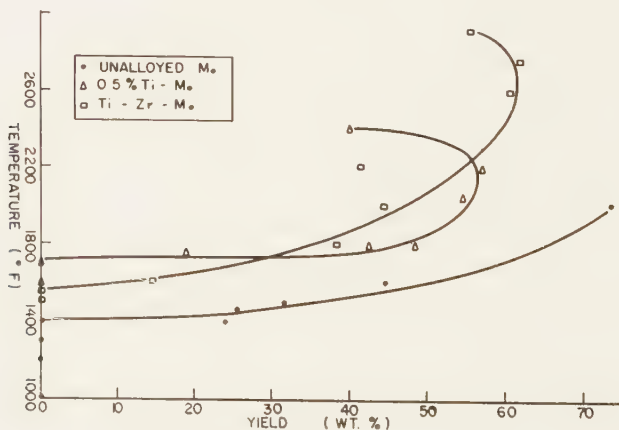


Fig. 3. Weight % yield vs. temperature.

All the data are based on a 6.0 in. $\times$ 3.125 in. diam. billet. The lubricants used on the billets consisted of glass powders having a viscosity in the range of 100–300 poise.

the extrusion temperature. The lubricant was applied by rolling the hot billet on fiberglass pad impregnated with glass of the proper viscosity. Hot work steel with a hardness 60 to 65 Rc proved to be the best die material. As a result of this work the die design has evolved from a flat face die to one that has a 90° included angle. Fig. 4 shows the die and billet in both uncoated and coated condition. A fiberglass pad is also used in the die face to give the billet its initial lubrication.



Fig. 4. Billet and die in coated and uncoated conditions.

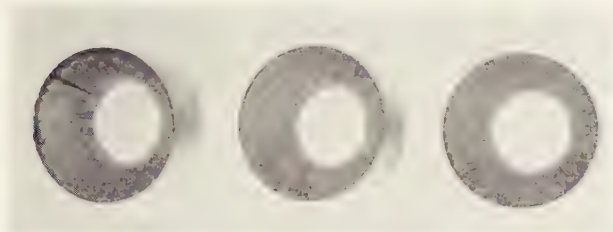


Fig. 5. Sandblasted dies, showing damage due to use at high temperature (1,430°–1,600°C).

Even though the glass acts as a lubricant, the high temperatures that are required to extrude the molybdenum alloys have a detrimental effect on the dies. Fig. 5 demonstrates how extensive the damage to dies is in the temperature range 1,430°C to 1,600°C. In the extrusion of billet MTZ1 (0.45% Ti–0.07% Zr–Mo) at 1,600°C the die face and bearing surface were washed to such a degree that the tail of the extrusion could not clear the aperture of the bolster. In order to improve the temperature capability of a die, a 0.015–0.020 in. layer of Al_2O_3 is flame-sprayed on its face. The Al_2O_3 coating has extended the operating temperature range of the die to 1,880°C.

Dies are not the only problem encountered in the temperature range of $1,370^{\circ}$ – $1,930^{\circ}\text{C}$. The problem of heating the billet to these high temperature requires specially designed furnaces. At the present time a vertically mounted induction coil which has a maximum temperature capability of $2,040^{\circ}\text{C}$ is used (Fig. 6).

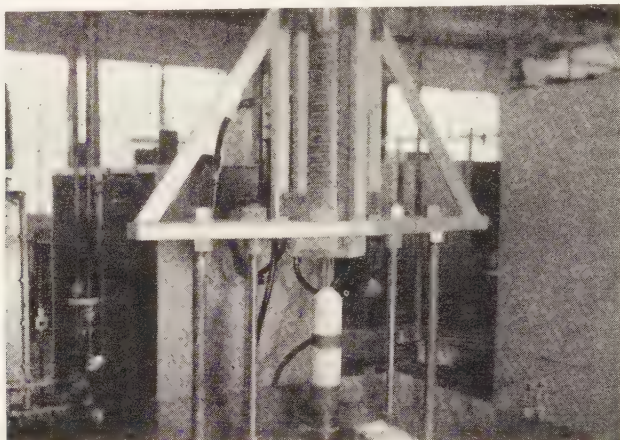


Fig. 6. Induction coil, with billet in position.

The tungsten work that has been accomplished thus far consisted of extruding sintered tungsten and tungsten molybdenum alloys. The main problem with the sintered material was that the density of the material did not appear to be improved at the 4 : 1 reduction ratio. An interesting point was the ability to extrude tungsten as easily with a steel can as without. Usually the steel can was used because the tungsten billet was too small for the container.

One programme was run on arc-cast tungsten molybdenum alloys which had been previously extruded at a 2 : 1 extrusion ratio. It was possible to extrude these billets in the temperature range of $1,290^{\circ}\text{C}$ to $1,520^{\circ}\text{C}$. The billets were canned in mild steel with a 0.250 in. wall thickness. Cans heated to 540°C were placed in the container and then the hot tungsten billets were placed in them immediately before extrusion; during the process the steel cans acted as lubricants.

Once wrought materials having useful strength and ductility are produced, it is of great interest to know how they would perform in an actual application. Such information is being made available on the Refractory Metals Structural Development Programme¹¹. This is intended to provide the answers to the problems which arise when one attempts to build and test a load-carrying airframe part of a refractory metal. The ultimate test component must be capable of efficient operation under stress in an oxidizing atmosphere at $1,370^{\circ}\text{C}$. Initially the programme was concerned with materials evaluation. This was primarily due to the lack of good quality sheet and of mechanical property data upon which to base an intelligent design. For the purpose of selecting the final alloy the following criteria were used:

- (1) high temperature tensile strength
- (2) oxidation resistance
- (3) ductility

- (4) availability
- (5) formability
- (6) weldability
- (7) coatability.

uitable samples of sheet were obtained for laboratory tests. The compositions and condition of these alloys are shown in Table V. One of the most important criteria was high temperature strength and so elevated temperature tensile tests were conducted on these alloys in a vacuum of 1μ at a strain rate of 0.005 in./in./min. The data for these alloys are shown in Table VI.

TABLE V
POTENTIAL ALLOYS FOR AIRFRAME COMPONENTS

Commercial designation and nominal composition	Gauge (in.)	Condition
F48 (Cb-15% W-5% Mo 1% Zr-0.03% C)	0.040	Stress-relieved, 1,204°C, 1 h
Mo-0.5% Zr	0.040	Stress-relieved, 1,204°C, 1 h
FS-82 (Mo-0.5% Ti-0.07% Zr- 0.04% C)	0.050	Stress-relieved, 1,204°F, 1 h
FS-82 (Cb-33% Ta-0.7% Zr)	0.070 and 0.020	Stress-relieved, 1,040°C, 1 h

TABLE VI
TENSILE PROPERTIES

Sample test conditions	F48		FS-82		1/2 Zr-Mo		TZM	
	UTS (p.s.i.)	3/4 in. Elong.	UTS (p.s.i.)	3/4 in. Elong.	UTS (p.s.i.)	3/4 in. Elong.	UTS (p.s.i.)	3/4 in. Elong.
Room temp.	121,800	15.9	81,600	11.3	108,000	18	134,000	13.8
371°C	27,300	47.2	11,850	53	38,650	13.8	26,800	31.9
Notched room temperature $K_t = 7.3-8.3$	105,600	1.5	81,900	3.0	116,700	2.0	135,750	2.0
1,371°C anneal test at 1,204°C	39,700	28.2	—	—	47,400	8.1	—	—
-17.8°C	126,150	17.8	112,350	15.5	115,900	5.8	—	—
-40°C	130,800	16.9	112,500	16.2	110,000	2.5	—	—

The F-48 alloy and the Mo-0.5% Zr alloy have the highest strength at 1,370°C. The FS-82 alloy is the lowest strength alloy, and its high density presents an added penalty in its use. Notched tensile tests also shown in Table VI indicated that the ratio of notched to unnotched tensile strength of all the alloys was near or greater than one, with the exception of the F-48 alloy, which had a ratio of 0.88. The effect of a 1,370°C anneal was evaluated and the ductility of the Mo-0.5% Zr alloy was significantly lowered. Data obtained in low temperature tensile tests are shown in Table VI. The F-48 alloy was ductile down to -40°C and the FS-82 alloy exhibited

good ductility with only a slight increase in tensile strength with decreasing temperature. No tests were made on the TZM alloy.

TABLE VII
NOTCHED ROOM TEMPERATURE TENSILE STRENGTH OF COATED SAMPLES

Alloy	Coating	K_t	U.T.S. (p.s.i.)	Elong. (%)	Ratio notched to unnotched strength
F48	Al diffusion coat	4.1	102,500	2	0.84
FS-82	Cr plate	5.7	51,600	2.5	(1)
TZM	Cr plate	4.1	39,000	Broke in pinhole	—
0.5 Zr-Mo	W-2 coating	4.4	103,000	Not measured	0.95
0.5 Zr-Mo	Cr plate	4.4	66,700	Broke in pinhole	—

(1) Cr plate heat treatment recrystallized the FS-82 and therefore reduced the tensile strength.

The best available coatings were applied to tensile test samples and the effect of the coating for each alloy was determined and is shown in Table VII. These tests indicated that the molybdenum alloys were embrittled by the 0.002 in. chromium plate. The tensile samples shattered into several pieces and fracture started at pinholes in the specimens rather than at the notch. The Chromalloy W-2 coated molybdenum alloy showed slight notch sensitivity. Subsequent bend tests showed one of the samples of W-2 coated molybdenum to be severely embrittled.

Room temperature bend tests were also conducted and the results for all the alloys except FS-82 are shown in Table VIII. FS-82 alloy was not subjected to this test because of a lack of material. However, from past experience it is expected that FS-82 alloy would have excellent bend ductility in all test directions.

TABLE VIII
ROOM TEMPERATURE BEND TESTS

Alloy	Specimen orientation	Die radius (in.)	"r"	Springback from 105°	Remarks
TZM	Longitudinal	0.0937	2.2	10°	Satisfactory
TZM	Transverse	0.0937	2.2	9°	Satisfactory
TZM	Longitudinal	0.0156	0.4	4°	Satisfactory
TZM	Transverse	0.0156	0.4	4°	Satisfactory
Mo-0.5 Zr	45°	0.0937	2.2	—	Fractured at 10° bend
Mo-0.5 Zr	Longitudinal	0.0156	0.4	—	Fractured at 25° bend
Mo-0.5 Zr	Transverse	0.0156	0.4	—	Fractured at 55° bend
F-48	Longitudinal	0.0937	2.2	12°	Satisfactory
F-48	Transverse	0.0937	2.2	15°	Satisfactory
F-48	Longitudinal	0.0156	0.4	7°	Satisfactory
F-48	Transverse	0.0156	0.4	7°	Cracked at 105° bend
F-48	45°	0.0156	0.4	10°	Slight crack on surface

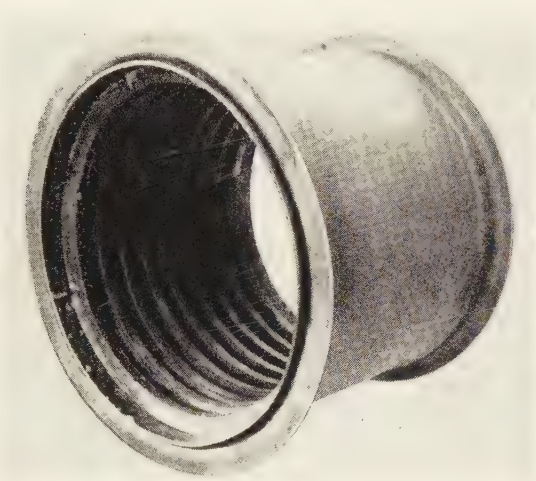


Fig. 7. Columbium test cylinder (before test).

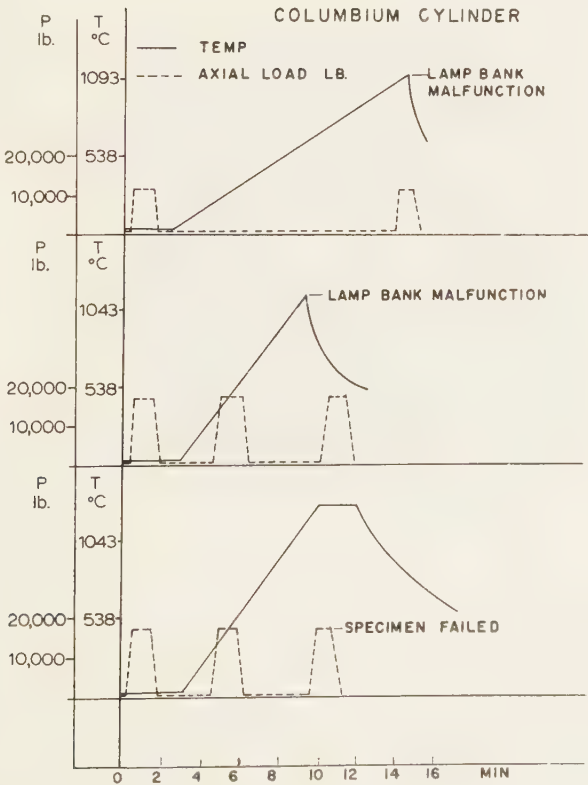


Fig. 8. Temperature and load sequence for columbium cylinder.

The alloy ultimately selected for fabrication of the final component was F-48 alloy. Since the strength levels of the F-48 and Mo-0.5% Zr alloys were acceptable for use in the final structural component, the choice of the alloy was based primarily on oxidation behaviour, ductility and weldability. The molybdenum base alloys showed advantages over columbium base alloys with respect to strength and availability. However, they have the disadvantage of a high ductile-to-brittle transition temperature as shown by the bend and tensile tests. Although weldability has not been discussed here, it is well known that ductile fusion welds can not be obtained with the molybdenum alloys. The columbium alloys do show promise of ductile fusion welds but insufficient data are available to be presented at this time.

During the materials evaluation phase a concurrent programme is being carried out to build and test various small scale design configurations to learn more of the problems involved.

A typical test configuration is shown in Fig. 7. This cylinder was fabricated from FS-82 columbium alloy and has been joined by fusion and resistance welding. The part was chrome plated on the outside prior to testing horizontally in compression and the temperature was maintained by a clam shell arrangement of quartz lamps on the external circumference of the cylinder. Fig. 8 illustrates the sequence of events in testing the cylinder and the time and load required for failure. A photograph of the failed cylinder is shown in Fig. 9.



Fig. 9. Columbium test cylinder (after test).

It is too early to draw conclusions from our structural development programme on the usefulness of refractory metals in hot structures. It is evident that more effort is required to establish confidence in these materials. Many alloys are available which have extremely high strength in inert atmosphere or vacuum. These properties become meaningless when a structure is required to operate in an oxidizing atmosphere. The problems of uniformity of properties, formability, coatability, and the choice of design criteria are also extremely important and in the final analysis determine the ultimate application. The U.S. Air Force is devoting additional development effort

these areas, and it is anticipated that refractory metals will someday take their place as useful structural materials.

ACKNOWLEDGEMENTS

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